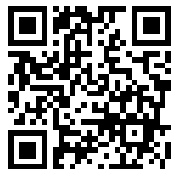


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AND

WILLIAM FRANCIS, F.L.S.

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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster  
vilior quia ex alienis libamus ut apes." *Just. Lips. Polit. lib. i. cap. 1. Not.*

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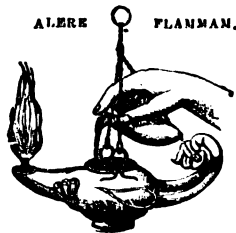
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perspicua . . . . Admiratio generat quæstionem, quæstio investigationem,  
investigatio inventionem."—*Hugo de S. Victore.*

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—“Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condât,  
Quid toties diros cogat flagrare cometas,  
Quid pariat nubes, veniant cur fulmina cœlo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu.”

*J. B. Pinelli ad Mazonium.*

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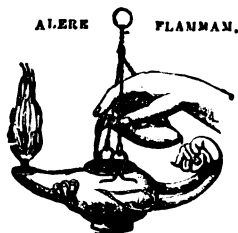
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Cur caput obscura Phœbus ferrugine condât,  
Quid toties diros cogat flagrare cometas,  
Quid pariat nubes, veniant cur fulmina cœlo,  
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I. *On the Electric Discharge through gases at very low pressures.* By Sir J. J. THOMSON, O.M., F.R.S.\*

IN this paper I consider some properties of the discharge at low pressures, especially those which are associated with the neighbourhood of the cathode, such as the dark space and the distribution of potential through it, the origin of cathode and positive rays, and the formation of the negative glow. My experiments were made at pressures comparable with those occurring in X-ray tubes with cold cathodes.

Let us first consider the sources of ionization in the dark space. I think the evidence is against this ionization being due, wholly or mainly, to the detachment of electrons by collisions of cathode rays or positive ions against the molecules of the gas.

We begin by considering the ionization due to the electrons driven from the cathode. Glasston's experiments (Phil. Mag. Oct. 1911) show that, as is indicated by theory, the number of ions produced by a cathode ray per unit length of path varies inversely as the kinetic energy of the ray. For rays moving with a velocity of  $4.7 \times 10^9$  cm./sec. through air at a pressure of 1 mm. of mercury, he found that 1.5 pairs of ions were produced by each ray in travelling over 1 cm. Under the usual conditions in gases at pressures where the dark space is well developed the velocity would be greater than this and the pressure much less than one

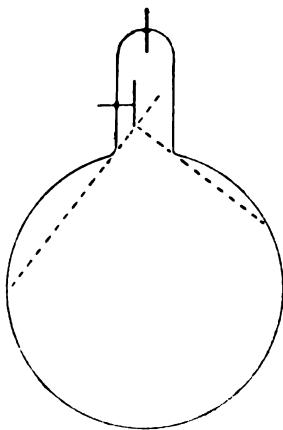
\* Communicated by the Author.

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millimetre, there would therefore be very little ionization by the electrons in passing over the dark space. Glasson (Proc. Roy. Soc. Tasmania, pp. 1-4, 1913) showed that the loss of energy by the electrons in their path is many times greater than can be accounted for by the work spent in ionization. This suggests that these high-speed electrons when passing through the molecules of a gas may displace some of the electrons in the inner layers of these molecules without ejecting them from the molecule. The return of these electrons to their old position would be accompanied by the emission of high frequency radiation which could ionize molecules on which it fell. Thus on this view the molecules traversed by the high-speed electrons emit radiation able to produce ionization. This radiation will spread throughout the surrounding gas, which will thus be exposed to ionizing radiation if it is within uninterrupted sight of a high-speed cathode ray. We suppose that the gas in this condition forms the negative glow, the luminosity of which is due to the recombination of the ions; when this recombination is prevented by a strong electric field as in the dark space, the gas is not luminous.

Fig. 1.



A confirmation of this view is afforded by the fact, long ago pointed out by Goldstein, that the negative glow, a region where there is very intense ionization and where the electric force is very small, extends to parts of the tube not traversed by cathode rays. Thus in a tube like that in fig. 1, taken from Goldstein's paper, Wied. Ann. lxxvii. p. 83 (1899), the negative glow extends to the region bounded by the

dotted lines. Thus, though the negative glow occurs in parts of the tube not traversed by cathode rays, it is confined to those parts which have an uninterrupted view of some part of the path of a cathode ray; this is in accordance with the view that it is due to radiation from the molecules of gas traversed by cathode rays. It is not necessary that the parts of the tube where the cathode rays are developed should have an uninterrupted view of the place where the cathode ray strikes the walls of the tube, so that this ionizing radiation is not exclusively that produced by the impact of cathode rays against solid bodies.

The existence of radiation other than luminous and X-ray radiations has been known for a long time: thus E. Wiedemann (*Zeitschr. f. Elektrochemie*, p. 159, 1895) showed that rays which could excite thermoluminescence, "Entladungstrahlen," are given out by electric sparks; the properties of these rays have been investigated by Hoffmann (*Wied. Ann.* lx. p. 269, 1897) and Miss Laird (*Phys. Review*, xxix. p. 225; xxx. p. 293). The writer (*Proc. Cambridge Phil. Soc.* x. p. 74, 1899; xiv. p. 417, 1907; xv. p. 482, 1908) has shown that in the discharge at low pressures rays occur which have the power of ionizing gases, and that the intensity of emission of these rays varies from one part of the discharge to another. The radiations inside the tube which cannot pass through its walls are deserving of much more attention than they have received. One kind of such radiation which can easily be observed occurs at comparatively high pressures, say about 1 mm., when if the tube is made of soft German glass an olive-green phosphorescence, quite different from that due to cathode rays, appears on the walls of the tube when the discharge passes. I have shown that this radiation can be refracted so that it is probably so near the luminous spectrum that it can be regarded as a form of ultra-violet light.

### *Ionization produced by Positive Ions.*

I do not think that the kind of ionization which results in the detachment of a free electron is often produced by the collisions of positive ions in the dark space. Such collisions cannot lead to ionization of this type unless the energy of the ions is exceedingly large, greater than some 70,000 volts if the ions are atoms of oxygen or nitrogen. As the energy must be proportional to the mass of the ions, for heavy ions it would far exceed that available with moderately sized coils.

There are two sets of considerations, one experimental the other theoretical, which lead to this conclusion.

The experimental evidence is, that the cathode rays after passing through the dark space all move at the same speed. Now, if ionization was going on in the dark space electrons would start from different parts of it and their kinetic energy when they were ejected from it would depend upon the place from which they started, and along with their kinetic energy their deflexions in electrostatic and magnetic fields would vary with their place of origin. Thus a narrow pencil of cathode rays formed by such electrons would spread out into a band when exposed to electric and magnetic forces. A similar pencil of cathode rays, if it consisted of electrons which had started from the cathode itself, would not spread out as all the electrons would have the same energy and suffer the same deflexion. Thus the study of the effect of electric and magnetic fields can give us a great deal of information about the ionization going on in the dark space, and I have made a large number of experiments on this subject.

The method adopted was as follows. A cathode with a plane face was placed in a side tube A, fused on to a large bulb; the cathode rays passed across the bulb and fell upon a metal plug with a hole bored through it placed at the junction with the bulb of another side tube B diametrically opposite to A. One of the very fine copper tubes used in positive ray experiments passed through the hole in the plug; the cathode rays leaving this tube formed a narrow pencil and passed through electric and magnetic fields of the type used to produce a positive ray spectrum. After passing through these fields the pencil fell on a Willemite screen at the end of the tube B, and in the absence of electric and magnetic forces produced a small circular patch of phosphorescence on the screen. When either the electric or magnetic field was in action the spot was deflected; it was not drawn out into a band, but remained a circular patch of the same size as the undeflected one with a very faint tail. This shows that the electrons which produce the phosphorescence are all moving at the same speed and that the effect on the screen of electrons moving at any other speed is negligible. By measuring the electrostatic deflexion of the rays we can deduce their kinetic energy, and can then compare it with the potential difference between the anode and cathode of the discharge-tube as determined by the equivalent spark-gap.

I have made experiments with different gases—air, hydrogen, oxygen, carbonic acid—and at different pressures,

and with the equivalent spark-gaps ranging from 2 to 35 millimetres; in all but a few exceptional cases to be considered later, the spot preserved its shape, it was not drawn out into a band, and the energy of the cathode rays as determined by their electrostatic deflexion was within the limits of the error inherent to the spark-gap method equal to that corresponding to the potential difference between the electrodes. In some cases when the "break" in the primary circuit of the induction-coil was working irregularly, there were several deflected spots to be seen; these were isolated and not connected by any band of luminosity, they were evidently due to changes in the potential differences between the terminals of the induction-coil due to the irregularities of the break.

The other reason for believing that ionization is not due to the collisions made by the positive particles follows from the consideration of the amount of energy that would be transferred to an electron by a collision with a positive ion. In consequence of the great mass of the ion in comparison with that of an electron, the energy of an ion if its speed were equal to that of an electron which possessed energy equal to the ionizing potential would be very much greater than that of the electron. Thus if the ionizing potential of the gas were 10 volts, the energy of a hydrogen molecule moving at the speed of an electron with the ionizing potential would be 36,000 volts, that of an atom of oxygen 288,000 volts, and so on. Thus, unless the velocities of the ions are much greater than those produced by ordinary induction-coils, the individual electrons in the ion possess far too little energy for them to be able to ionize as individuals.

Let us now consider the transference of energy from the ion to an electron, regarding the ion as a unit. If  $M_1$ ,  $M_2$  are the masses of two colliding particles, one of which may be regarded as at rest,  $T$  the kinetic energy of the moving one, the transfer of energy from the one particle to the other is

$$\frac{4M_1M_2}{(M_1 + M_2)^2} T \sin^2 \theta,$$

where  $2\theta$  is the angle through which the direction of the relative velocity of the particles is deflected by the collision; hence the maximum amount of energy which can



be transferred is

$$\frac{4M_1M_2}{(M_1 + M_2)^2} T,$$

or when, as in the case we are considering, one of the masses  $M_1$  is small compared with the other,

$$\frac{4M_1}{M_2} T.$$

Thus an atom of hydrogen could only transfer 4/1800 of its energy to an electron, so that if the ionizing potential were 10 volts it would have to have energy represented by 4500 volts to detach the electron; if the ion were an atom of oxygen its energy would have to be 72,000 volts. Thus the energy of all ions, except hydrogen and possibly helium, would have to be far greater than those available with the use of ordinary coils if they are to produce ionization by collisions. At very low pressures with large potential differences between the electrodes, it is possible that in hydrogen and helium we may have cathode rays with less than the normal energy. In a few cases I have observed that the pencil of cathode rays was spread out into a band by the electric and magnetic fields; this may have been due to hydrogen ions, which are nearly always present in the discharge through rarefied gases.

There is, however, another and very interesting way in which positive ions can produce ionization. When these ions reach the cathode they give up their charges to the electrode and become neutral. This neutralization is produced by an electron falling into the positive ion. Now, when an electron falls into an atom radiation is emitted; this radiation is done up into units, each unit possessing an amount of energy measured by the loss of potential energy due to the fall of the electron into the atom. When the electron falls into and neutralizes a positive ion, this energy is equal to the ionization potential of the neutralized ion, *i.e.* to the ionization potential of the atoms or molecules of the gas through which the discharge is passing. Thus, when a positive ion is neutralized, radiation is emitted which has enough energy when absorbed to ionize the atoms or molecules of any gas whose ionizing potential is ever so little less than that of the gas which supplied the ion. Thus at the cathode where the positive ions are neutralized, radiation is emitted which has all but enough energy to ionize the gas itself; this radiation will fall upon the metal of the cathode and give rise to photoelectric effects, as the energy per unit of

radiation necessary for these effects is less than that corresponding to the ionization potential of most gases. The electrons liberated by the photoelectric effects will start from close to the cathode, and thus when they emerge from the dark space will form a homogeneous system having energy represented by the full fall of potential in the dark space. The radiation which is not absorbed by the metal of the cathode will go out into the gas and will be able to ionize any molecule upon which it falls if the ionizing potential of the molecule is less than that of the ion.

Thus positive ions, though of insufficient energy to ionize by direct collision, may through the radiation they emit when they are neutralized produce ionization, which may extend over a volume large compared with that which could be reached if the ionization were due to collision.

It may be noted in this connexion that Horton and Davies (Proc. Roy. Soc. xcv. p. 333) have detected the emission of electrons from a metal plate struck by positive helium atoms with energy as low as 20 volts.

The sequence of events in the dark space is thus as follows :—

- (1) The positive ions emit radiation when they give up their electrical charges at the cathode; this radiation we call radiation (i).
- (2) Radiation (i) falling on the cathode causes a photoelectric emission of electrons from the electrode.
- (3) These electrons acquire a high speed under the electric field, and then when traversing the molecules of the gas cause them to emit a radiation which we call radiation (ii).
- (4) Radiation (ii) ionizes those portions of the gas which it can reach before it is absorbed.
- (5) The recombination of the ions thus produced gives rise to the luminosity of the negative glow; this recombination consisting of the falling in of an electron to a positive ion will produce radiation which can ionize molecules whose ionizing potential is less than that of the neutral atom formed by the recombination. We shall call this radiation, radiation (iii).

Thus on this view there are several kinds of radiation near the cathode : there is radiation (i) starting from quite close to the cathode, (ii) starting from all regions traversed by the cathode rays, and (iii) coming from the negative glow.

The number of electrons ejected from the cathode by the action of radiation (i) may depend upon the energy possessed by the positive ions when they strike against the cathode as well as upon the number of such ions. For just as in the motion of positive rays through gases when a positive ion may get neutralized and then again positively charged by giving up an electron to a molecule against which it strikes, so a positive ion striking against the cathode may alternate from the charged to the uncharged condition, if it has much energy, many times before it loses its charge for the last time : each change from the positively charged to the uncharged state would be accompanied by the emission of radiation. The type of radiation (i) might be expected to depend mainly upon the nature of the positive ions ; the number of ions ejected by the radiation would depend to some extent upon the kind of material used for the cathode.

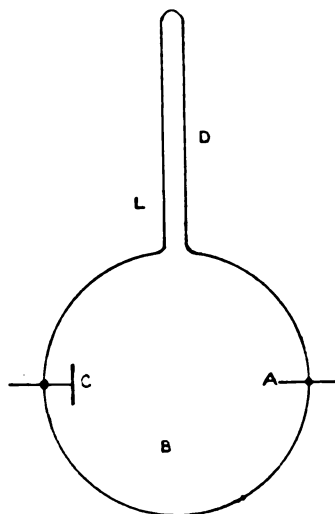
With regard to radiation (ii), the type of this radiation, *e. g.* its frequency and penetrating power, would depend on the energy the cathode rays possess when they excite it and also upon the nature of the molecules which are excited by the rays. As the energy of the cathode rays varies from point to point of their path, this radiation will not be homogeneous. The maximum energy of the cathode rays depends upon the current through the tube and the pressure of the gas, so that the properties of this kind of radiation will be a function of the pressure and of the current. The amount of radiation excited per cm. of path will be proportional to the pressure of the gas, and as the absorption of the radiation is also proportional to the pressure, if the cathode rays extend through a considerable volume of the gas the intensity of radiation (ii) at any point will not vary much with the pressure. As radiation (ii) is excited by cathode rays having considerable momentum part of which they lose when exciting this radiation, we should expect the momentum of the radiation to be in the same direction as that of the cathode rays, so that more of this radiation would travel forward in the direction of the cathode rays than would travel back.

The type of radiation (iii) which arises from the recombination of the ions produced by radiation (ii) will depend mainly upon the character of the gas in the tube. It is of greater wave-length than (ii), not extending much below 1000 Ångström units.

*Nature of Radiation (ii).*

The following experiment throws, I think, some light on the nature of this radiation. B (fig. 2) is a large bulb with a cathode at C and an anode at A; D is a long narrow tube about 50 cm. long. Within a certain range of pressure the negative glow extends right up to the top of D. A strong electromagnet was placed at L: when this magnet was in action the negative glow in D was not affected except in the region close to L; here it was extinguished, and the glow

Fig. 2.



formed two luminous columns separated by a short non-luminous layer. The ends of the luminous column showed much the same relation to the magnetic force acting upon them as does the luminous boundary of the dark space when acted on by magnetic force. Though the magnetic field produced this local disturbance, the upper part of D remained filled with glow whose brightness did not seem much affected by the magnetic field. This experiment shows, I think, that radiation (ii) does not in the main consist of secondary cathode rays, for if it did the rays could not have crossed the magnetic field at L unless their velocity had been considerably greater than the primary cathode rays. I conclude then that radiation (ii) is in the main radiation of the character of light or Röntgen rays, and not a corpuscular radiation.

*Production of Positive Ions in the Dark Space.*

Positive ray photographs show that a narrow pencil of positively charged atoms or molecules of one kind, *e.g.* atoms or molecules of hydrogen, is drawn out into a continuous band when the rays are acted on by electric or magnetic forces; showing that there are some atoms whose energy is equal to  $E$  where  $E$  may have any value between certain wide limits. This is in contrast to the behaviour of the cathode rays, for we have seen that except in very special circumstances practically all the high-speed electrons possess the same amount of energy. It is natural to attribute the variation in energy of the positive ions to their having been produced at different parts of the dark space and having, therefore, on their arrival at the cathode fallen through varying potential differences. If, however, the process which produces the positive ion was the dissociation of an atom or molecule into an electron and positive part, the electrons on leaving the dark space would also have fallen through varying potential differences, would possess different energies, and a pencil of cathode, like one of positive rays, would be drawn out into a continuous band by electric and magnetic fields.

There are two processes by which we could get charged positive ions without electrons. The first is by the impact of a positive ion on a diatomic molecule, of which one atom may be regarded as positively, the other as negatively electrified. Now, though the collision of a positive ion with a molecule could not, unless the energy of the ion were exceedingly large, separate an electron from the molecule, it might, if the molecule consisted of two oppositely charged ions, separate these ions, and dissociate the molecule into a positive and a negative ion. It could do this because the masses of these ions are much more nearly equal to its own mass than is the mass of an electron, so that a much greater fraction of the energy of the positive ray could be communicated to the ion than to the electron. Thus, while the fraction given to the electron would be too small to detach it, the fraction transferred to the ion might be large enough to tear it away. The fact, however, that the variation of the energy of the positive rays occurs in monatomic gases like helium and argon as well as in diatomic ones, shows that this cannot be the only way in which the variation of the energy of the positive rays can be produced. Though a positive ray might not be able to detach and set free an electron from a molecule with which it came in contact, it

might in virtue of its charge be able to capture an electron from a molecule against which it struck and carry it away. The electron would neutralize the positive ray, and leave the molecule or atom from which it had been captured positively electrified. The positive ray would not communicate its energy to this atom or molecule, so that this would start on its career as a positive ray with little or no energy; the potential difference it would have to pass through before it reached the cathode would be less than the full fall of potential across the dark space, so that its energy when it reached the cathode would be less than the maximum.

The neutralized atom would continue to move with a high velocity, and if it came into contact with a molecule of the gas through which it is passing might either carry an electron away or leave one behind; in either case a pair of ions would be produced. The repetition of this process might give rise to a considerable number of positive and negative ions, but not to any electrons.

We can obtain an integral equation to determine the potential in the dark space under such conditions. Let  $\phi(x)$  be the potential at a distance  $x$  from the luminous boundary of the dark space. Let  $\lambda$  be the average distance traversed by an ion before transferring its charge to another. Then the chance of this transference taking place between  $\xi$  and  $\xi + d\xi$  is

$$e^{-\frac{\xi}{\lambda}} \frac{d\xi}{\lambda},$$

and the chance that the ion passes through a distance  $x$  without transferring its charge is  $e^{-\frac{x}{\lambda}}$ .

If a positive ion starts from rest at a point  $\xi$ , its velocity when it reaches  $x$  will, if there is no loss of energy, be equal to

$$\sqrt{(2e/M)\{(\phi(x) - \phi(\xi))\}},$$

where  $M$  is the mass of the ion. Hence if  $i_0$  is the number of ions starting from near the luminous border of the dark space per second and therefore  $i_0 e^{-\frac{\xi}{\lambda}} \frac{d\xi}{\lambda}$  the number which start from the layer between  $\xi + d\xi$  and  $\xi$ , the density of positive electricity at  $x$  will, if we neglect the effect of ions which have experienced more than one transference of charge, be

$$e i_0 e^{-\frac{x}{\lambda}} + e i_0 \int_0^x \frac{e^{-\frac{\xi}{\lambda}} d\xi}{\lambda \sqrt{(2e/M)(\phi(x) - \phi(\xi))}}.$$



The density of electricity is  $\frac{1}{4\pi} \frac{d^2\phi}{dx^2}$ , and since the density of the negative electricity is small compared with that of the positive, we may equate these expressions and get an integral equation for  $\phi(x)$ ; this I have not been able to solve except when  $\lambda = \infty$ , when  $\phi(x) = (9\pi i_0 e)^{2/3} x^{4/3}$ .

We can see, however, that since the transference we are considering diminishes the average velocity of the ions when they approach the cathode, it will increase the density of the positive electricity near the cathode and thus make the force increase more rapidly in that region than the distribution of potential represented by  $x^{4/3}$ , the law when each ion reaches the cathode without interruption.

If an appreciable fraction of the current is carried by positive ions, then at low pressures and with fairly large currents all the molecules of the gas in the discharge-tube may have to strike against the cathode many times per second. Thus if the pressure is .01 mm. of mercury and the current through the tube carried by the positive ions is one milliamper, in one second  $10^{-4}$  electromagnetic unit of electricity or  $3 \times 10^6$  electrostatic units must be given up at the cathode. As the charge on an ion is  $4.77 \times 10^{-10}$  electrostatic units, a charge of  $3 \times 10^6$  units requires  $6.2 \times 10^{15}$  ions. In one centimetre of gas at .01 mm. at  $0^\circ \text{C}$ . there are  $2.75 \times 10^{19} / 760 \times 10^2$ , or  $.36 \times 10^{15}$  molecules; hence in one second the molecules contained in about 17 c.c. of the bulb must come in contact with the cathode. Unless this flow of ions to the cathode is balanced by a backward flow of molecules, the pressure at the cathode end of the tube must increase continually.

To produce this backward flow the pressure must increase as we approach the cathode. Taking the case of a plane cathode at right angles to the axis of  $x$ , then if  $n$  is the number of molecules per c.c. at a distance  $x$  from the cathode, the flow of molecules from the cathode due to the pressure gradient is per unit area per second

$$-\frac{dn}{dx} \cdot D,$$

where  $D$  is approximately  $\frac{1}{3}\lambda c$ , where  $\lambda$  is the free path of the molecule and  $c$  the average velocity of translation of the molecules. If this flow is to balance that of positive ions towards the cathode, then if  $i$  is the current per square centimetre carried by the positive ions,

$$\frac{i}{e} = \frac{c}{3} \lambda \frac{dn}{dx}.$$

In consequence of the large value of  $D$  at low pressures a very small pressure gradient is sufficient to produce a flow which will balance the flow of gas caused by the motion of the ions. Thus to take the numerical case just considered where  $i/e = 6.2 \times 10^{15}$ , suppose that  $c$  equals  $4.6 \times 10^4$ , the value for a molecule of oxygen at  $0^\circ \text{C}$ . Then

$$1.5 \times 10^4 \lambda \frac{dn}{dx} = 6.2 \times 10^{15},$$

$$\text{or} \quad \lambda \frac{dn}{dx} = 4.1 \times 10^{11}.$$

At a pressure of  $.01 \text{ mm}$ .  $n$  will be of the order of  $3.5 \times 10^{14}$ , so that

$$\lambda \frac{dn}{dx} = \frac{n}{850} \quad \text{approximately.}$$

Thus a gradient in the number of molecules which only amounted to a change of one part in about 850 in a length equal to the free path would be sufficient to counterbalance the pressure effects of the flow of positive ions to the cathode.

On the view that the main supply of the positive ions comes from near the luminous boundary of the dark length, we should expect that the backward flow of the uncharged molecules would be confined to the dark space, as such a flow would be sufficient to keep things in a steady state. The backward flow in addition to uncharged molecules may contain (see 'Rays of Positive Electricity,' p. 134) negatively charged molecules, and "retrograde" positively charged ones, though the number of these is small in comparison with the flow of positive ions to the cathode or of uncharged molecules away from it.

It is important to consider whether the values of current and potential observed when discharges pass through gases at low pressures are compatible with the view that the potential difference is that calculated from the distribution of positive electricity through the dark space. The lines on which the potential can be calculated are those given on p. 11, and although we cannot get an exact solution for the potential in that case, it is easy to see that the order of magnitude of the potential will be the same as that for the effect of a space-charge when all the electrons come from one electrode. In this case

$$i = \frac{\sqrt{2}}{9\pi} \sqrt{\frac{e}{M}} \frac{V^{3/2}}{x^2}, \quad \dots \dots (1)$$

where  $i$  is the current per unit area of the electrode,  $V$  the

potential difference, and  $x$  the distance between the electrodes;  $M$  the mass of the carrier of the electric charge. All the quantities are measured in electrostatic units.

We shall in applying this formula to the discharge through rarefied gases take  $x$  as the thickness of the dark space and  $V$  the potential difference across that space;  $i$  will be the density of the current carried by the positive ions, not the total current through the tube. Let us take the case when  $V$  is 30,000 volts, in electrostatic measure 100, and when the thickness of the dark space is 6 cm. If the carriers of the positive electricity are atoms of hydrogen  $e/M = 3 \times 10^{14}$ ; hence by (1)  $i = 10^8/4$  in electrostatic units or  $1/120$  ampere, *i. e.* about 8 milliamperes. If the current were carried by atoms of nitrogen instead of hydrogen,  $i = .57$  milliampere. These values of  $i$  are high considering that  $i$  is only the part of the current carried by the positive ions and is probably but a small fraction of the total current. At higher pressures, when the discharge passes more easily, the values of  $i$  are much smaller and do not seem necessarily incompatible with the magnitude of the currents flowing through the tube.

It must be remembered that the interpretation of such an equation as that we have just quoted depends upon the answer to two questions, neither of which has been definitely settled :

- (1) Is the discharge at these low pressures continuous even when a constant difference of potential is applied to the electrodes?
- (2) Is there an abrupt change in potential at the cathode?

With regard to (1) it is evident that if the discharge is intermittent the real value of  $i$  when the discharge is passing may be very much greater than the average value recorded by an ammeter. Dauvillier has found that the discharge through an X-ray bulb is intermittent even when a constant potential difference is used to drive the bulb. From general considerations we might, I think, expect variations in the current even under constant potential. For even when a gas is in a steady state, if absolutely instantaneous photographs could be taken of its molecules, there would be no resemblance between the photographs taken at different times; on the other hand, if the time of exposure were considerable in comparison with the time of relaxation, there

would be but little difference between successive photographs. Thus we see that it is only for effects which extend over a time longer than the time of "relaxation" of the gas that we can regard the gas as being in a "steady" state; for shorter times both the gas and the effects must be regarded as variable. In the discharge through gases at low pressures, the time it takes for an electron or charged atom to cross the dark space may be but a very small fraction of the time of "relaxation" of the gas; the gas cannot be regarded as in a "constant" state for these electrical effects, and the variation in the state of the gas may produce variations in the intensity of the current under a constant potential difference.

The evidence with regard to (2) is contradictory at moderate pressures: Westphal finding that there is a considerable drop of potential close to the cathode, while Aston finds no trace of any abrupt change in the potential. If such a drop exists, then equations of the type of (1) connecting potential and current cannot be applied, until we know how much of the potential is used up close to the cathode.

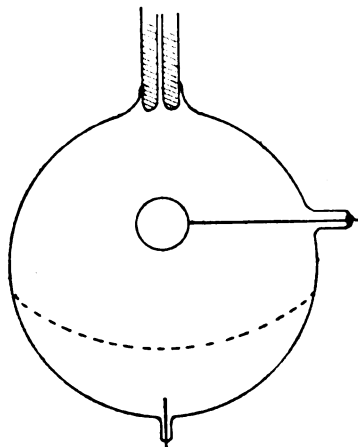
Another important point on which we have at present no direct information is the proportion between the current carried by the positive ions and that carried by the electrons. The fact that in X-ray bulbs the heating effect at the anticathode—the place bombarded by electrons—is very much greater than that at the cathode itself—the place bombarded by the positive ions—suggests that much the greater part of the current is carried by electrons. We shall see that this view is helpful in explaining many of the properties of the discharge at low pressures.

The question arises as to where the positive ions are produced. Are they produced in the positive column and drift into the dark space where they get accelerated, or are they produced in the dark space itself? The following experiment shows, I think, that a considerable quantity at any rate are produced in the dark space itself. In the tube used to take positive-ray photographs a quartz bulb was placed in front of the cathode at about the middle of the dark space (fig. 3); if the positive ions all drifted in from the cathode they would be stopped by the quartz bulb and no positive-ray photographs would be produced, as a matter of fact excellent photographs were taken with the quartz bulb in this position.

We shall suppose that ionization takes place in the dark space but that the number of ions produced in this region is much less than the number of electrons which start from the cathode; thus by far the greater number of electrons which

emerge from the dark space will possess the maximum energy corresponding to the fall through the whole potential difference in the dark space, while the energy of the positive ions which strike the cathode will vary with their place of origin in the dark space.

Fig. 3.



We shall now proceed to apply these ideas to some of the properties of the discharge at low pressures; we shall begin with the formation of the dark space.

We have supposed that the ionization in this space is due to the radiations (i), (ii), (iii). Let  $q$  be the intensity of the radiation and  $\rho$  the density of the gas; the rate of ionization per unit volume will be  $k\rho q$ , where  $k$  is a quantity which does not depend upon  $\rho$  or  $q$ . If the intensity of the radiation is constant throughout the dark space, and if  $d$  is the thickness of that space, the rate of ionization in the dark space estimated per square centimetre of the cathode is  $k\rho qd$ , and since there is no recombination in the dark space this will be the number of positive ions which strike against the unit area of the cathode per second. The emission of electrons from the cathode is on our view due to the neutralization of the positive charges; it will be proportional to the number of such charges and to their energy when they reach the cathode; the average energy will be proportional to the cathode fall of potential  $V$ . Thus if  $\gamma$  is the number of electrons emitted per second per unit area of cathode,

$$\gamma = Ak\rho qdV, \quad \dots \dots \dots (2)$$

where  $A$  may depend upon the nature of the ions and the material of which the cathode is made.

We have supposed the ionization to be due to radiation primarily excited by the passage of the cathode rays through the gas; the intensity  $q$  of this radiation will therefore be proportional to  $\gamma$ . The energy communicated to a molecule by an electron whose energy is  $V$  is proportional to

$$\frac{aV}{c+bV^2}.$$

The energy communicated to the molecules per unit path will also be proportional to  $\rho$  the density of the gas; on the other hand, the absorption of the radiation by the gas will also be proportional to  $\rho$ , so that if we are dealing with the radiation from a large volume of gas the intensity of the radiation reaching any point will not vary much with  $\rho$ . Hence we may put

$$q = B\gamma \cdot \frac{aV}{c+bV^2},$$

where  $B$  is a quantity which in general does not vary rapidly with  $\rho$  but may do so under special conditions. Substituting this value of  $q$  in (2) we get

$$1 = B A k \rho d \cdot \frac{aV^2}{c+bV^2},$$

$$\text{or} \quad \rho d = \frac{1}{B A k} \left( \frac{b}{a} + \frac{c}{aV^2} \right) \quad . \quad . \quad . \quad . \quad (3)$$

Thus when  $B$  is independent of  $\rho$ , the thickness of the dark space is given by an equation of the form

$$\rho d = C + \frac{D}{V^2},$$

where  $C$  and  $D$  are constants if the tube and the nature of the gas with which it is filled remain unaltered.

The distribution of potential in the dark space may be calculated as follows, provided the potential depends only upon the distance from the cathode:—

Let  $\phi(x)$  be the potential difference between the luminous boundary of the dark space and a place  $P$  at a distance  $x$  from it. The positive charge at  $P$  will have travelled to it from places like  $Q$ , whose coordinates  $\xi$  are less than  $x$ . If a positive ion started from  $Q$  and fell freely to  $P$  its velocity at  $P$  would be equal to

$$\sqrt{\frac{2e}{M}(\phi(x) - \phi(\xi))}, \quad . \quad . \quad . \quad . \quad (4)$$

where  $M$  is the mass of the positive ion. If  $\tau$  is written for *Phil. Mag.* S. 6. Vol. 48. No. 283. July 1924. C



$kqp$ , the number of positive ions which start per second from a layer of thickness  $d\xi$  at  $Q$  is  $rd\xi$ . The density of these when they reach  $P$  will be  $rd\xi/v$ , where  $v$  is written for the expression (4); hence the density of the positive charge at  $P$  is

$$e \int_0^x \frac{rd\xi}{v}.$$

As the negative electricity is carried by electrons which move much more quickly than the positive ions, the density of the negative electrification will be negligible in comparison with that of the positive. Hence the resultant density of the electrification will be practically that of the positive charges, so that

$$\frac{1}{4\pi} \frac{d^2\phi}{dx^2} = e \int_0^x \frac{rd\xi}{v} = r \sqrt{\frac{Me}{2}} \int_0^x \frac{d\xi}{\sqrt{\phi(x) - \phi(\xi)}}, \quad (5)$$

an integral equation to find  $\phi(x)$ . To solve it put  $\phi(x) = Ax^n$ , when equation (5) becomes

$$\begin{aligned} \frac{A}{4\pi} n(n-1)x^{n-2} &= r \sqrt{\frac{Me}{2}} \int_0^x \frac{d\xi}{x^{\frac{n}{2}} \sqrt{1 - \left(\frac{\xi}{x}\right)^n}} \\ &= r \sqrt{\frac{Me}{2}} \frac{1}{x^{\frac{n}{2}-1}} \int_0^1 \frac{dz}{\sqrt{1-z^n}}. \end{aligned}$$

Thus

$$n-2 = -\left(\frac{n}{2}-1\right)$$

or  $n=2,$

and  $A^{3/2} = r\pi^2 \sqrt{\frac{Me}{2}},$

so that

$$\phi(x) = (r\pi^2 \sqrt{Me/2})^{2/3} x^2; \quad \dots \quad (6)$$

so that if  $d$  is the thickness of the dark space and  $V$  the potential difference across it,

$$V = (r\pi^2 \sqrt{Me/2})^{2/3} d^2.$$

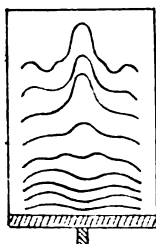
If  $I$  is the current carried by the positive ions  $erd = I$ , hence

$$V = \pi^{4/3} \left(\frac{M}{2e}\right)^{1/3} I^{2/3} d^{4/3}.$$

The distribution of potential represented by equation (6) is that found by Aston (Proc. Roy. Soc. lxxix. p. 526) ; his experiments were, however, made at comparatively high pressures and with small potential differences.

The equipotential surfaces corresponding to this solution are planes parallel to the cathode. Wehnelt has shown however, that in consequence of the electrification on the walls of the tube the discharge tends, even with large cathodes, to concentrate at the centre of the cathode and the equipotential surfaces are distorted into the shapes represented in fig. 4.

Fig. 4.



We see from the expression for  $V$  that when the potential across the dark space is given, the thickness of the dark space varies inversely as the square root of the current.

The following calculation illustrates the effect of pressure and of the volume occupied by the negative glow on the value of  $q$  the intensity in the dark space of the ionizing radiation. Suppose that a unit of this radiation is liberated at  $P$  by a cathode ray, let  $\lambda$  be the mean free path of this unit, i. e.  $\lambda$  is the average distance the unit travels before it ionizes a molecule. Let  $\delta v$  be an element of volume at a point  $Q$ ; then if  $\delta\omega$  be the solid angle subtended by  $\delta v$  at  $P$ , the chance that the unit of radiation will start in the right direction to reach the element of volume at  $Q$  is  $\delta\omega/4\pi$ . If  $r$  is the distance of  $Q$  from  $P$ , the chance that the unit of radiation will ionize a molecule while going through the distance  $dr$  near  $Q$  is  $e^{-\frac{r}{\lambda}} \frac{dr}{\lambda}$ ; hence the chance that the ray from  $P$  ionizes in the volume  $\delta v$  is

$$\frac{\delta\omega}{4\pi} e^{-\frac{r}{\lambda}} \frac{dr}{\lambda},$$

or, since  $r^2 \delta\omega \delta r = \delta v$ ,

$$\frac{e^{-\frac{r}{\lambda}} \cdot \delta v}{4\pi r^2 \lambda}.$$

The number of ions produced per unit volume in the dark space by a single unit of radiation is thus  $e^{-r/\lambda}/4\pi r^2\lambda$ . If these rays are produced uniformly throughout the negative glow, and if  $n_0$  is the number of such rays starting from unit volume per second, the ionization per second per unit volume at Q will be

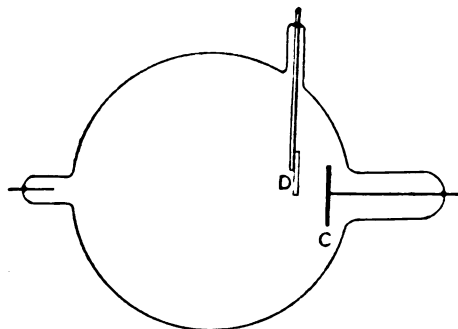
$$\frac{n_0}{4\pi} \iiint \frac{e^{-r/\lambda}}{r^2\lambda} \cdot r^2 dr \sin \theta d\theta d\phi,$$

where the integration is extended over the region traversed by the cathode rays. Performing the integration we find for the ionization the value

$$\frac{n_0}{4\pi} (1 - e^{-L/\lambda}) \Omega,$$

where  $\Omega$  is the solid angle subtended at Q by the region traversed by the cathode rays, and  $L$  the value of  $r$  at the outer boundary of this region. This is the quantity we denoted by  $kq\rho$ ;  $n_0$  the number of units of radiation produced per unit volume by the cathode rays will be proportional to  $\rho$ , thus  $q$  will be proportional to  $(1 - e^{-L/\lambda})$ ; if  $L/\lambda$  is considerable  $q$  will be independent of both  $L$  and  $\lambda$  and hence of  $\rho$ , and hence by equation (3),  $\rho d$  will be independent of  $\rho$  except in so far as  $c/aV^2$  involves  $\rho$ . If however  $L/\lambda$  is small,  $q$  will be proportional to  $L/\lambda$ ; and since  $1/\lambda$  varies as  $\rho$ ,  $q$  will be proportional to  $\rho$ , and  $\rho^2 d$  and not  $\rho d$  will be constant. A case in which the length of the dark space varies with the pressure more rapidly than  $1/\rho$  is that represented in fig. 5.

Fig. 5.



C is a plane cathode from which cathode rays travel horizontally and strike against an insulated piece of plate glass D.

The bulb is for the most part filled with negative glow, but in addition to the usual dark space in front of the cathode there is another dark space in front of D not in general of the same thickness as that in front of C.

The negatively charged cathode rays starting from C carry a definite current into the plate D; as this plate is insulated, when things have settled down into a steady state, an equal current must flow back from D across the dark space in front of it. As this space is dark there is no recombination of the ions within it, so that the current through it will be saturated and measured by the number of ions produced in this space per unit time; it is also equal to the current carried by the cathode rays which strike D, so that the ionization in this dark space, like that in front of C, will be directly proportional to the number of cathode rays coming from unit area of C. The region which can send ionizing radiation to the dark space in front of D is much smaller than that which can send such radiation to the dark space at C, so that while the thickness of the dark space at C should vary as  $1/\rho$ , that at D should vary more rapidly with the pressure.

I made a series of measurements of the relative thicknesses of the primary dark space at C and the secondary one at D at different pressures; the gas in the bulb was oxygen, because the negative glow is denser and the outline of the dark space more sharply defined than in any other gas I have tried. The results are given in the following table.

Primary dark space at C.	Secondary dark space at D.
20 mm.	1.5 mm.
25 mm.	2.5 mm.
28 mm.	3.5 mm.
35 mm.	5.0 mm.
45 mm.	7.0 mm.

It will be seen from these numbers that as the thickness of the dark space at C increases as the pressure diminishes, that at D increases still more rapidly. If, as many experiments indicated, the thickness of the cathode dark space varies as  $1/\rho$ , that of the dark space at D must vary as a higher power of  $1/\rho$ . The measurements are consistent with this thickness varying as  $(1/\rho)^2$ .

*The Negative Glow.*

We shall consider in more detail the properties of the negative glow. This luminous glow forms the outer boundary of the dark space, its appearance and the volume through which it extends depend upon many factors such as the pressure of the gas, the current through the tube, the shape of the tube, the paths of the cathode rays through it, and the nature of the gas in the tube. In the negative glow the electric force is exceedingly small in comparison with its value in other parts of the tube, indicating that there is very intense ionization in the glow. This ionization, on the view we have suggested, is produced primarily by the radiation (ii) given out by molecules of gas traversed by cathode rays; the ions and electrons produced in this way recombine, and in doing so give out luminous radiation and a radiation corresponding in energy to the ionizing potential of the system formed by the electron and positive ion after recombination. Thus in a mixture of ions of different ionizing potentials, the recombination of those with a high ionizing potential will give out radiation capable of producing a fresh supply of the ions with a smaller ionizing potential. The ionization in the negative glow is not merely the detachment of an electron from a molecule: if this were so, all the positive ions would be molecules; the evidence of the positive rays shows that these molecules are often broken up into atoms and that these atoms may combine and form new compounds. Thus, though only one kind of compound gas be put in the discharge-tube, we find on analysis by positive rays that there may be twenty or thirty different kinds of carriers of positive electricity due to new arrangement of the atoms which were in the molecules of the compound gas.

The conditions in the negative glow seem to be those of thermodynamic equilibrium, *i. e.* if the gas filling the tube is a compound containing say oxygen, hydrogen, and carbon atoms in certain proportions, then in the negative glow there will be all possible compounds of these elements, and these compounds will be in the proportions corresponding to thermodynamic equilibrium at a suitable temperature.

We know that in many cases the elements are able to exist in stable equilibrium in proportions which bear no relations to those indicated by thermodynamics. Thus, mixtures of hydrogen and oxygen in the proportion of two volumes of hydrogen to one of oxygen will exist side by side at room temperatures without the occurrence of any chemical combination, whereas thermodynamical considerations would

indicate that practically all the atoms should be united in  $H_2O$ .

The reason that thermodynamic equilibrium is not attained under ordinary conditions is, to take the example just considered, that before  $H_2O$  can be formed from a mixture of  $H_2$  and  $O_2$ , work has to be expended to split the oxygen molecules into atoms. Although the final result of the formation of water from hydrogen and oxygen results in a great liberation of energy, yet, before this result can be obtained, there must be a preliminary expenditure of energy and there must be some sources from which this energy can be borrowed. To lend this energy is the function of a catalyst, and anything which can supply the energy sufficient to enable the reaction to start on a small scale will act as a catalyst. Now, in the negative glow we have many sources of energy which are not present in gases in the normal state. We have energy stored up in radiations of various kinds, we have the energy of moving electrons : all these will act as catalysts and enable the gases in the negative glow to be in thermodynamic equilibrium. I have made a good many experiments to test whether or not this is so. The method was as follows : I filled the discharge-tube with, say, carbon monoxide and obtained the positive-ray spectrum, then I pumped out the CO and filled the tube with  $CO_2$ , and again obtained the positive-ray spectrum. There were differences between the spectra of CO and  $CO_2$ , but these were not so much in the absence or presence of lines corresponding to different atoms or molecules, for as a matter of fact if a line is present in one of these spectra, traces at least of it are found in the other ; the differences in the two spectra are in the relative intensities of the lines ; this, however, might be because the proportion between the number of carbon atoms and of oxygen ones is not the same in CO as in  $CO_2$ . When, however, oxygen is mixed with CO in the proportion of one volume of oxygen to two of CO, so that the mixture is represented by  $2CO + O_2$ , the proportion between the carbon and oxygen atoms is the same as for  $CO_2$ . On comparing the positive-ray photograph of the mixture with that of  $CO_2$ , I could not detect any differences between them. I made similar experiments with formaldehyde  $COH_2$  and the mixture  $CO + H_2$ , with methyl alcohol  $CH_3.OH$  and the mixture  $CO + 2H_2$ , with formic acid  $CHO.OH$  and the mixture  $CO_2 + H_2$ , and found that in each of these cases the positive-ray spectrum of the mixture was the same as that of the compound. This is the result we should get if



the gas in the negative glow were in thermodynamic equilibrium at a high temperature, for the composition of a mixture of carbon, oxygen, and hydrogen atoms in thermodynamic equilibrium depends at a given temperature only upon the number of atoms of carbon, oxygen, and hydrogen, and not upon their state of combination when introduced into the discharge-tube.

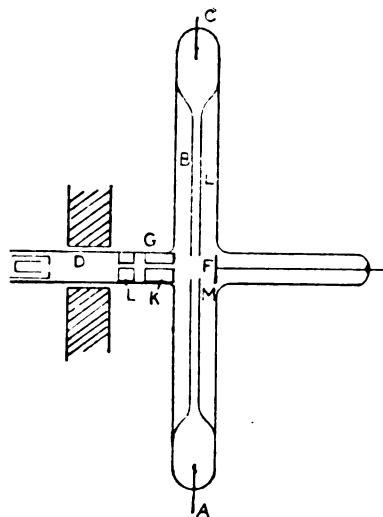
Incidentally we may mention that the positive-ray photographs of carbon compounds, and especially of such compounds as benzene, phenol, and hydrocyanic acid, show that in the negative glow carbon has a great tendency to polymerize, for in the positive-ray photographs of these gases we find lines corresponding to  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_5$ .

It takes only a very short time for the gas in the discharge-tube to settle down into thermodynamic equilibrium when the electric discharge is passing through it. This is shown by the fact that the lines corresponding to the different atoms or molecules appear on photographs taken with the "instantaneous" discharge. The "instantaneous" discharge is that produced when the induction-coil which produces the discharge is not allowed to run continuously. Instead of using the ordinary interrupter to break the primary circuit, the primary circuit is broken by hand, using a break with a very strong spring so as to make the interruption of the circuit as abrupt as possible. I found that a spring gave as abrupt a break as Lord Rayleigh's method of breaking the primary circuit by a bullet fired from a revolver, and was much more convenient. I was not able to get the discharge sufficiently intense to photograph a single flash, but what was equivalent to a photograph of a single flash was obtained by passing a steady stream of the gas under investigation through the discharge-tube and making the interval between the flashes so long that all the gas that was in the bulb when one flash was taken was washed out before the next flash. I got distinct photographs with twenty or thirty flashes, and these showed lines corresponding to a great variety of atoms and molecules, showing that these were produced in the time taken by the flash. I estimated from the results given by Professor Taylor Jones for a coil of somewhat similar dimensions that the duration of each discharge was about  $1/3000$  sec. Each of these flash discharges shows all the usual characteristics of the discharge through gases at low pressure, *e. g.*, the dark space, the negative glow, and the positive column.

*The Ions in the Positive Column.*

In the part of the luminous discharge which is in contact with the anode, the electric field is very much weaker than it is in the dark space ; and this part of the discharge can be shielded easily from the radiations which we have supposed to produce the ionization in the negative glow and the dark space. The ionization in the positive column we regard as due to ionization by the collisions of electrons ; it is therefore a matter of some interest to investigate the nature of the ions in the positive column to see whether they approach in variety and complexity those which pass through the dark space and are revealed by positive ray analysis. I have made experiments on this point, and though the research is not yet complete evidence has been obtained that the character of the ions in the positive column is similar to that of those in the positive rays, though we are not yet in a position to say that the ions are the same in all respects.

Fig. 6.



The method used to investigate the ions in the positive column is that indicated in fig. 6. The current from an induction-coil passed from the cathode C to the anode A, through two glass tubes L and M separated by an interval and adjusted so that the axes of the tubes were in the same straight line. The positive column filled the greater part of

these tubes and stretched across the interruption between them. The nature of the ions in the interval between the tubes was investigated in the following manner. The glass tube G carries a tightly-fitting metal plug K with a hole bored through it, a long fine copper tube of the kind used in my experiments on Positive Rays fitted tightly into this hole. One end of this tube came opposite the interval between the tubes L and M. This fine tube was the only channel of communication between the vessels B and D, so that by means of powerful pumps and charcoal cooled with liquid air a good vacuum could be maintained in D, even when the pressure in D was comparable with that due to a millimetre of mercury.

To drive the positive ions from the positive column through the narrow tube in the plug, an electric field was maintained between the side electrode F and the plug K. After passing through the fine tube the ions were accelerated before passing through a hole in another plug L. After going through L they pass between the poles of an electromagnet and then pass through a circular hole in a closed brass vessel, behind this hole is a Faraday cylinder connected with a Dolezalek electrometer. The potential differences required to drive the ions through the tube and accelerate them afterwards were derived from a high potential dynamo made by Evershed and Vignolles which gave steady potential differences up to 6000 volts. The current from this dynamo ran through two high resistances—two tubes A and B filled with a mixture of xylol and alcohol. A was inserted between F and K, B between K and L. The resistance of A is small compared with that of B, so that the energy which the ions possess when they pass through the magnetic field is very nearly that due to the potential difference between the terminals of the dynamo, and is the same for all ions. The deflexion by the magnetic field of an ion whose mass is  $m$  and velocity  $v$  is equal to

$$\frac{e}{mv} B,$$

where  $B$  is a quantity which depends upon the strength of the magnetic field and upon the length of path traversed by the ion before it reaches the aperture in front of the Faraday cylinder.  $B$  was determined by the method given in my 'Rays of Positive Electricity,' 2nd edition, p. 18. If  $V$  is the potential difference between the terminals of the dynamo,

then approximately

$$\frac{1}{2}mv^2 = Ve;$$

hence the deflexion of the ion is equal to

$$\left(\frac{e}{m}\right)^{1.2} \frac{B}{\sqrt{2V}} \dots \dots \dots (7)$$

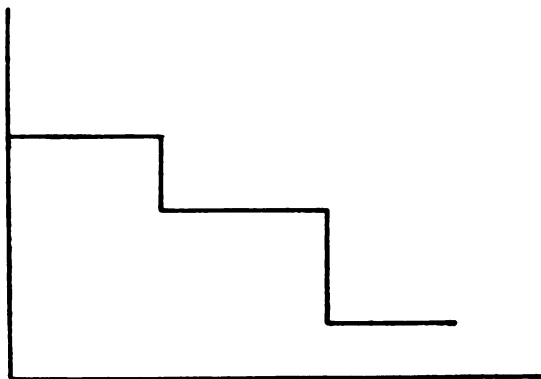
Let us now consider what is the effect of gradually increasing the magnetic field on the charge of positive electricity received by the Faraday cylinder and measured by the electrometer. The apparatus is adjusted so that when there is no magnetic field the ions pass through the centre of the aperture in front of the Faraday cylinder. No effect on the charge received by the cylinder will be produced until the deflexion of the most deflected ion (the atom of hydrogen) is equal to the radius of the circular aperture in front of the Faraday cylinder.

When the magnetic force reaches a value just large enough to produce this deflexion, the charges which were carried to the Faraday cylinder by the atoms of hydrogen are stopped by the walls of the vessel round it, and the deflexion of the electrometer falls—abruptly if the pencil of rays is very narrow, gradually if it is diffuse. After this diminution in the deflexion of the electrometer there will be no further diminution until the magnetic force reaches the value for which the deflexion of the ion next in mass to the hydrogen atom, *i.e.*, the hydrogen molecule, is equal to the radius of the aperture; at this stage there will again be a sudden diminution in the deflexion of the electrometer. Thus we see that if we plot the deflexion of the electrometer as ordinate against the magnetic force as abscissa, we should with a very narrow beam of positive ions get a graph like fig. 7.

Each nick in the graph indicates the presence of an ion, which under the magnetic force represented by its abscissa is deflected through a distance equal to the radius of the aperture. Knowing this radius and the magnetic force, we can from the expression (7) determine the value of *m* for each of the ions. In my experiments the beam of positive ions was widened by the scattering it experienced in its passage up to the Faraday cylinder, so that the nicks in the graph were rounded off and it was not possible to obtain more than approximate values of *m*. They were, however, sufficiently well marked to determine with ease whether or not a particular ion was to be found among those drawn

from the positive column. I have found in this way that in the positive column in air there are, even when the pressure approaches 1 mm. of mercury, atoms and molecules of hydrogen, atoms of either oxygen or nitrogen or both—the nicks due to these are too near together to be separated with certainty in my curves—as well as molecules of these elements. These experiments show that the ionization in the

Fig. 7.



positive column involves the splitting up of molecules into atoms as well as the abstraction of electrons from molecules. This suggests that in the positive column as in the negative glow we have a distribution of atoms and molecules analogous to that which represents thermodynamic equilibrium of the gases in the tube at a high temperature.

It is remarkable that these experiments show no traces of negative ions, as distinct from electrons, in the positive column; when the electrode F is made negative, instead of positive, so as to drive negative instead of positive ions into the Faraday cylinder, no appreciable deflexion of the electrometer occurs; though when the potential of F is reversed so as to drive positive ions into the cylinder, the electrometer may show a deflexion of more than 100 divisions in a minute.

#### *Theory of the Uniform Positive Column.*

We suppose that the ionization in the positive column is due, (1) to collisions with free electrons, (2) to radiation given out when a positive ion is neutralized by an electron falling into it. Positive and negative ions are supposed not to produce ions in the positive column by collision.

Let  $n_1, n_2, m$  be respectively the number of free electrons, of negative ions, and of positive ions per unit volume.

Let the average time taken by an electron to acquire under the electric force sufficient energy to produce ionization by collision and to effect the ionization be  $T$ , then the number of ions produced by collisions per second in unit volume is  $n_1/T$ . The ionization due to radiation will be proportional to the radiation emitted in unit time; this will be proportional to the number of positive ions neutralized in that time, *i. e.* to  $n_1 m$ . We shall suppose that the rate of production of ions from radiation is  $r n_1 m$ . Hence the total rate of production of electrons per unit volume is

$$\frac{n_1}{T} + r n_1 m.$$

This must be equal to the rate at which the electrons disappear; the electrons disappear by combining (1) with positive ions to form neutral molecules, (2) with neutral molecules to form negative ions. The rate of the first process is  $a_1 n_1 m$ , where  $a_1$  is the coefficient of recombination between electrons and positive ions; the rate of the second is  $a_2 n_1 \rho$ , where  $a_2$  is a coefficient of recombination and  $\rho$  the density of the gas in the discharge-tube. Hence equating the rate at which the electrons are produced to that at which they disappear,

$$\frac{n_1}{T} + r n_1 m = a_1 n_1 m + a_2 n_1 \rho \quad . . . . . (8)$$

The rate at which negative ions are produced is  $a_2 n_1 \rho$ , the rate at which they disappear is  $\alpha n_2 m$ , where  $\alpha$  is the coefficient of recombination of the positive and negative ions and  $n_2$  the number of negative ions per unit volume. Hence

$$a_2 n_1 \rho = \alpha n_2 m \quad . . . . . (9)$$

In the uniform positive column the electric force is constant, so that there can be no resultant electric charge at any portion of it. Hence

$$n_1 + n_2 = m \quad . . . . . (10)$$

From (8), (9), (10) we get

$$m = \frac{\frac{1}{T} - a_2 \rho}{a_1 - r} \quad . . . . . (11)$$

$$\frac{n_1}{\alpha m} = \frac{n_2}{a_2 \rho} = \frac{m}{\alpha m + a_2 \rho}.$$

If  $i$  is the current through unit area,  $u_1$ ,  $u_2$ , and  $v$  the velocities of the electrons, negative ions, and positive ions respectively, then

$$n_1 u_1 + n_2 u_2 + m v = \frac{i}{e},$$

or

$$\frac{\alpha u_1 m^2 + a_2 u_2 \rho m + \alpha v m^2 + a_2 v \rho m}{\alpha m + a_2 \rho} = \frac{i}{e}. \quad (12)$$

This is an equation to determine  $m$ , and when  $m$  is known  $1/T$  can be determined from (11). Now, as we shall see,  $T$  can be expressed in terms of the electric force  $X$ , so that (12) will lead to expression for the electric force.

When, as in the cases we are considering, the pressure is very low by far the greater part of the current is carried by the electrons. When this is so (5) reduces to

$$\frac{\alpha u_1 m^2}{\alpha m + a_2 \rho} = \frac{i}{e}.$$

For very small values of  $i$  this by equation (11) reduces to

$$\frac{1}{T} = a_2 \rho.$$

To find  $T$  we may proceed as follows. For the electron to ionize the gas by collision it must acquire under the electric field energy equal to that corresponding to the ionizing potential  $V$ . Let  $X$  be the electric force in the positive column,  $d$  the distance measured in the direction of the force through which the electron must move to acquire the energy corresponding to the ionizing potential, then, if there is no loss of energy at the collisions,

$$Xd = V.$$

The electron while moving through a distance  $d$  from the source will make many collisions. The chance that after  $n$  collisions the distance it has travelled is between  $\lambda x$  and  $\lambda(x + dx)$  is  $\frac{2}{n} e^{-\frac{x^2}{n}} x dx$ . (Rayleigh, 'Theory of Sound,' 2nd ed. vol. i. p. 40). The average distance is equal to

$$\begin{aligned} \frac{2\lambda}{n} \int_0^\infty e^{-\frac{x^2}{n}} x^2 dx \\ = \frac{1}{2} \pi^{1/2} \sqrt{n} \cdot \lambda, \end{aligned}$$

where  $\lambda$  is the mean free path of the electron. Hence  $n$  the

number of collisions it makes before it travels through a distance  $d$  may be taken as given by the equation

$$d = \frac{1}{2} \pi^{1/2} \sqrt{n} \cdot \lambda.$$

Since the free path of an electron moving through uncharged molecules is proportional to its velocity (Phil. Mag. xlvii. p. 345) the time between each collision is constant. Hence the time required to make these  $n$  collisions will be given by the equation

$$T = \frac{n\lambda}{v},$$

where  $v$  is the velocity and  $\lambda$  the free path of the unaccelerated ion. Now

$$n = \frac{4d^2}{\pi\lambda^2} = \frac{4}{\pi} \frac{V^2}{X^2\lambda^2},$$

hence

$$T = \frac{4}{\pi} \frac{V^2}{X^2\lambda^2} \frac{\lambda}{v}.$$

We now proceed to find  $a_2\rho$ ;  $1/a_2\rho$  is the average time taken by the electron to unite with a neutral molecule to form a negative ion. It follows from the theory of the recombination of ions (see Phil. Mag. xlvii. p. 360), and has been proved by the experiments of Loeb (Phil. Mag. xliii. p. 229) that an electron makes many collisions before uniting with a molecule to form a negative ion. Let  $N$  be this number, which has been measured by Loeb for several gases, then

$$\frac{1}{a_2\rho} = \frac{N\lambda}{v}.$$

Since, when the current is small

$$T = \frac{1}{a_2\rho},$$

$$\frac{4}{\pi} \frac{V^2}{X^2\lambda^2} = N,$$

$$\text{or} \quad X\lambda = \frac{2}{\sqrt{\pi}} \cdot \frac{V}{\sqrt{N}}.$$

The free path we are concerned with here is the path of a charged electron. In consequence of the charge  $\lambda$  will be shorter than the geometrical free path  $L$ , which is equal to  $1/\rho\pi\sigma^2$ , where  $\sigma$  is the radius of the uncharged molecule.



It can be shown (Phil. Mag. xlvii. p. 345) that

$$\frac{\lambda}{L} = \frac{1}{2 \cdot 2} \sqrt{\frac{\beta\theta}{U}},$$

where  $\beta\theta$  is the average energy due to thermal agitation of a molecule of the gas at the absolute temperature,  $\theta$ , and  $U$  the work required to deprive a negatively electrified molecule of its electron. Hence

$$XL = \frac{4 \cdot 4V}{\sqrt{\pi}} \sqrt{\frac{U}{N\beta\theta}}.$$

This equation is obtained on the supposition that  $i$  the current is very small.

When  $i$  is finite we have by (12)

$$\frac{\pi X^2 \lambda^2}{4 V^2} = \frac{1}{N} + (a-r) \frac{\lambda}{v e u_1}.$$

The fact that an electron makes a very large number of collisions before it gets attached to an uncharged molecule reduces the electric force required to make an electron ionize the gas to a value much below that which would be required if the electron only made a few collisions when in the free state. For example, if the electric force is such that  $X\lambda = V/10$ , where  $X$  is the electric force and  $\lambda$  the mean free path, then, if the electron only makes one collision when in the free state, the chance of its getting enough energy to ionize is the chance of describing without collision a distance 10 times the mean free path, i. e.,  $\epsilon^{-10}$ , a very small quantity. If it, on the other hand, makes  $10^4$  collisions in a free state, and if these collisions are elastic, the chance that after making these collisions the electron would have enough energy to ionize the gas is

$$\epsilon^{-10^4} \quad \text{or} \quad \epsilon^{-\frac{1}{10^4}},$$

which is very nearly a certainty.

### Summary.

The paper contains a theory of the electric discharge at low pressures based on the view that the ionization in the dark space and in the negative glow is due (1) to the radiation emitted when the positive ions are neutralized at the cathode, this radiation by its photoelectric effect causes an emission of electrons from the cathode; these electrons fall through

the whole potential difference in the dark space and constitute the high-speed cathode rays. Experiments are described which prove that all the cathode rays have nearly the same energy, differing in this respect from the positive rays which have energies ranging over wide limits.

The direct ionization due to the collision of high-speed cathode rays is, as Glasson's experiments show, small at their low pressures, but though these rays in their passage through the gas do not liberate many electrons, they cause the molecules through which they pass to emit a radiation which ionizes the surrounding gas in the negative glow and the dark space, the luminosity of the glow being the result of the recombination of electrons and positive ions produced in this way. The recombination of these electrons and positive ions also gives out a radiation which can ionize gases whose ionizing potential is less than that of the neutral atom or molecule formed by the combination of the electron and positive ion.

The positive ions, except in light gases like hydrogen and helium, will not, unless the potential differences are of the order of sixty-five thousand volts for the oxygen atom and higher for other gases in proportion to their molecular weights, produce free electrons by collisions. This is due to the great differences between the masses of the ions and the electrons, which makes it impossible for more than a fraction of the energy of one to be transferred to the other by a collision.

An expression for the distribution of potential in the dark space is deduced from these principles; according to this expression the potential difference between a point in the dark space and the negative glow is proportional to the square of the distance of the point from the edge of the glow. This is the result arrived at by Dr. Aston in his experiments on this subject. An expression is also obtained for the connexion between the thickness of the dark space and the pressure of the gas.

Experiments are also described on the character of the ions in the positive column, and an expression found for the electric force in a uniform unstriated column.

II. *On the Helmholtz Theories of the Struck String.*—  
Part II. *Experimental.* By W. H. GEORGE, B.Sc.,  
Research Student, University College, Nottingham\*.

[Plates I.-III.]

**I**N a previous paper (Phil. Mag. xlvii. pp. 591-602 (1924)) the Helmholtz theories of the struck string were considered, and in order to subject the second theory to quantitative experimental test expressions were there deduced for quantities whose magnitude could be determined from a displacement-time curve of the struck point of the string. In the present paper the apparatus used for obtaining experimentally the required displacement-time curves is described together with the results obtained. As the apparatus has been used to investigate a number of problems of the struck string, it will be described here in such detail as to serve the purpose of future papers as well as the present one.

#### DESCRIPTION OF APPARATUS.

*The String.*—The steel piano wire used is stretched on a monochord for lengths up to 100 cm. and across bridges (B) fixed upon roof-posts of the laboratory for lengths up to 316 cm. Two advantages of the use of the long string are, first, the greater range of available values of the ratio of the mass of the hammer to the mass of the string ( $m/M$ ), and, second, the larger displacements obtained for a given mass ratio.

The exact striking place can be found by smoking the string before taking a record and allowing the hammer to strike once only. The bright speck caused by the removal of the black deposit at the striking place gives a clearly defined zero mark from which the distance of the nearer bridge can be measured. When a wedge-shaped metallic hammer-head is used an alternative method available consists in smoking the hammer face only. After a single impact a tiny black speck is left on the bright string and serves as the zero mark.

*The Hammer.*—Previous workers† have used the mechanism of the pianoforte key. The hammer used in the present research may be regarded as a compound pendulum

\* Communicated by Prof. E. H. Barton, F.R.S.

† Kaufmann, Wied. Ann. liv. (1895); Berry, Phil. Mag. xix. pp. 648-51 (1910), and xx. pp. 652-57, xxii. pp. 113-118 (1911).

to which simple calculations are applicable. Photographs of three types of these pendulums are shown in Pl. I, fig. 2. The shaft consists of a lath of wood at one end of which two boxwood side pieces are glued. These serve to support the steel axle which fits in a hole drilled accurately perpendicular to the plane of the lath. The method of suspension will be clear from the photograph. The hammer-head is usually fixed at two-thirds the length of the pendulum from the axle, in order to avoid violent reactions there. In some cases when it is desirable to reduce the mass of the pendulum, it is shortened and the hammer-head is fixed at the end. Wedge-shaped hammer-heads are made by folding and hammering aluminium or copper foil. They are each securely fastened to the shaft by two screws and nuts, so that relative motion between hammer-head and shaft is prevented. As these hammer-heads are not wide enough to cover the slit of light used in observing the motion of the struck point, pieces of foil are usually fixed on them so that, at the instant of contact, the foil is in a plane parallel to the plane of motion of the string and has one edge parallel to and vertically beneath the string. Any relative motion of the hammer-head and the string in or perpendicular to the direction of the string's length during the impact can be tested by previously smoking the string or the hammer-head. The felt-covered hammer-heads are machine made of the type used in pianofortes. The block of wood (A) from which the pendulums are suspended is secured to the cross-piece (C) by a single bolt and wing-nut so that the hammer strikes at any desired place along the string. The cross-piece (C) is adjustable in the two directions perpendicular to the string. It will be noted that the pendulum can be removed from the apparatus in order to study the damping with the suspension unaltered. The natural vibrations of the hammer-shaft can be studied by removing the pendulum from its suspension, withdrawing the steel axle, and clamping the boxwood side pieces in a heavy vice. Distortion of the hammer during the impact can be studied by instantaneous photography and also by evidence deduced from the displacement-time curve of the struck point.

*Optical Arrangements.*—Fig. 3 shows one portion of the optical arrangements. An arc and condenser serve to illuminate by a horizontal beam a vertical slit (S) formed by two safety-razor blades. This horizontal beam is changed to a vertical one by the prism (P) and a horizontal image of the slit is focussed by the lens (L) upon the string, the final image being perpendicular to the string. The whole of this

portion of the apparatus is carried by a platform which runs on rails (RR) parallel to the string. Referring now to fig. 1, the image of the slit, a portion of which is cut off by the string, is focussed by the lens (D) onto the photographic plate through a slit in the "camera." The magnification in the final image is  $5/3$ .

*The Camera.*—This consists of a long shallow wooden box having a groove along each of its two longer sides. In these two grooves a plate-holder (H) slides and is shot by stretched catapult elastic at uniform speed past a slit in the lid of the box, the elastic being just unstretched as the right-hand edge of the plate reaches the slit. A spring device at the right-hand end of the box prevents the rebound of the plate-holder past the open slit. In fig. 1 (Pl. I.) the box is shown with the lid open. In an actual experiment the box is taken into a dark-room and a plate is put in the holder which is pulled to the left-hand end of the box and there held by a brass pin which passes up through the bottom of the box and through a hole in the plate-holder. The lid of the box is then closed onto a felt pad which renders the box light-tight, and the box is removed from the dark-room and placed against stops on a platform which is set so that the plate travels parallel to the string. Special Rapid or Press plates of speed H & D 270-475 were used.

*Timing Arrangements.*—In order to obtain a record of the impact it is necessary to have some timing device which will ensure the arrival of the plate at the slit just before the hammer strikes the string. To facilitate this, two electromagnets (M and E) are used and are connected with a cell and a morse-key (K) so that when the key is depressed (i.) the circuit containing M is made, so releasing the hammer, and (ii.) the circuit containing E is broken, so releasing a weight which falls from an adjustable height ( $h$ ) upon a lath (F). Any timing required is attained by the corresponding adjustment of this height ( $h$ ) which can be approximately calculated, since the time of descent of the hammer can be obtained from its initial inclination with the vertical. The lath (F) is pivoted at one end and has at the other end a right-angled hook which fits into the brass pin of the camera previously mentioned. By this means the falling weight knocks out the pin and releases the plate.

The velocity ( $v_0$ ) of the hammer at the beginning of the impact is adjustable by varying the initial inclination ( $\beta$ ) of the hammer with the vertical. If the hammer-head is attached at two-thirds the length of the pendulum from the

axis of rotation, we have :

$$v_0 = \sqrt{2gr(1 - \cos \beta)},$$

where  $r$  is the distance between string and axis of rotation of the pendulum. If the hammer-head is attached at the end of the pendulum, then :

$$v_0 = \sqrt{3gr \frac{(m' + 2M')(1 - \cos \beta)}{(m' + 3M')}},$$

where  $m'$  is the ordinary mass of the hammer-shaft and  $M'$  is the mass of the hammer-head. When the apparatus is set for taking a record, the pendulum is held at the desired inclination with the vertical by the pin which rests upon a small cylindrical metal rod which in turn slides in bearings and has a piece of iron attached to the other end opposite to the electromagnet ( $M$ ). By this arrangement the pendulum rests under a minimum of constraint, so that when it is released by the electromagnet it descends to the string without vibrations having been set up in its shaft. During the impact we may regard the pendulum as vertical and its velocity as uninfluenced by the acceleration of gravity.

On the experimental displacement-time curves accompanying this paper (Pls. II. & III.) the time axis is horizontal and positive from right to left. On the original larger figures (*i. e.* Pl. II. figs. 1-9) 1 cm. along the time axis represents approximately 1/318 sec., whilst on the smaller figures (Pl. III. figs. 12-23) 1 cm. represents approximately 1/205 sec. The dark patch on each records the motion of the hammer which covers up the slit during the impact. From the inclination ( $\alpha$ ) with the time axis of the right-hand linear boundary of the patch the initial velocity ( $v_0$ ) of the hammer can be determined, and is given by

$$v_0 = V \tan \alpha / \text{magnification},$$

where  $V$  is the velocity of the plate. Similarly, the velocity of rebound ( $v$ ) of the hammer can be determined.

The graph paper effect appearing on some of the figures (Pl. III. figs. 16-19) is obtained by the use of a grid-plate as described in 'Nature' (vol. cxiii. p. 387 (1924)).

#### TEST OF APPARATUS.

Before applying the measurements to test the Helmholtz theory, it is desirable to compare them with similar measurements made by Kaufmann, whose work must be taken as

standard. In Table I. are given examples of the percentage differences between Kaufmann's experimental and theoretical values in a number of cases chosen by him to support his theoretical work.

TABLE I.

Page of Kaufmann's paper.	$l/a$ .	$m/M$ .	Quantity.	No. of Experi- ments.	% Difference.
693 .....	2	0.917	$\tau$	{ 1	- 4.58
694 .....	2	"	$\theta$	{ 1	- 5.93
695 .....	2	"		{ 1	-12.15
694 .....	2	"	$y/2$	{ 1	-19.4
696 .....	10	1.78		{ 5	+ 1.6 to + 2.4
" .....	{ 11.25 to 4.5	1.385	$\tau$	{ 4	-11.6 to + 2.8
" .....	20.4	{ 1.35 to 3.51	$\theta$	{ 3	- 5.06 to + 4.17
*697 .....	10.8	2.79		{ 5	- 2.5 to +18.8

No measurements given for  $y_2$  when  $l/a > 2$ .

\* Throughout the paper an asterisk denotes the use of a felt-covered hammer.

From the above table it is clear that in work of this nature large differences between experimental and theoretical values must be expected. This is due firstly to the large number of quantities to be measured, and secondly to the fact that in order to treat the problem theoretically at reasonable length a number of factors have to be omitted.

In Table II. experimental values obtained in the present work are compared with the corresponding values obtained from Kaufmann's theory. By the term "% Difference" is here meant

$$\frac{\text{Exptl. value} - \text{Theo. value}}{\text{Theo. value}} \times 100.$$

By comparison of the percentage difference columns in Tables I. and II. we may conclude that, although the apparatus differs from Kaufmann's, the results obtained with it are of the same order of accuracy as Kaufmann's results. It may be noted that in all cases it was found possible to obtain a second displacement-time curve identical with the first as tested by superposition of the negatives. Figs. 10 and 11, originally intended to illustrate two cases of this repetition of any desired curve, have been omitted for reasons of economy.

TABLE II.

Quantity.	Figure.	On Kaufmann's Theory.	By Experiment.	% Difference.
$\tau$	*1	0.567	0.57	nil
$\theta$	2	0.567	0.57	nil
	3	0.989	1.0	1
	4	0.637	0.633	-0.6
	5	0.381	0.355	-6.8
	6	0.244	0.243	nil
$t_2$	*1	0.50	0.50	nil
$\bar{\theta}$	2	0.50	0.51	2
	3	0.564	0.563	nil
	4	0.318	0.305	-4.0
	5	0.1907	0.17	-10.8
	6	0.124	0.115	-7.4
$y_2$	*1	0.895 cm.	1.0 cm.	11.7
	2	0.803	0.9	12.1
	3	3.55	4.1	15.5
	4	2.37	2.36	nil
	5	1.56	1.5	-4
	6	0.875	0.7	-20
$\frac{-v}{r_0}$	*1	0.66	0.696	5.5
	2	0.66	0.63	-4.5
	3	0.634	0.68	7.2
	4	0.691	0.69	nil
	5	0.7986	0.817	2.3
	6	0.450	0.4225	-6.1

## TEST OF HELMHOLTZ THEORY.

In the following two tables experimental values are compared with those predicted by the Helmholtz theory and also where possible with those predicted by the Kaufmann theory.

TABLE III.

Quantity.	Fig.	By experiment.	On Helmholtz Theory.		On Kaufmann Theory.	
			Theo. Value.	% Difference.	Theo. Value.	% Difference
$t_2$	*1	0.50	0.318	57	0.500	nil
	2	0.51	0.326	56	0.500	2
	3	0.563	0.562	nil	0.564	nil
	4	0.305	0.320	-4.7	0.318	-4
	5	0.17	0.189	-10.0	0.1907	-10.8
	6	0.115	0.1375	-16.3	0.124	-7.4
$y_2$	*1	1.0 cm.	2.68 cm.	-63	0.895 cm.	11.7
	2	0.9	2.46	-63	0.803	12.1
	3	4.1	4.17	-2	3.55	15.5
	4	2.36	2.25	4.9	2.37	nil
	5	1.5	1.647	-8.9	1.56	-4
	6	0.7	0.985	-29	0.875	-20



TABLE IV.

Quantity.	Fig.	By experi- ment.	On Helmholtz Theory.	% Difference.
$t_2$	7	0.312	0.2535	23
$\theta^*$	8	0.359	0.262	37
	9	0.575	0.5085	13
	*12	0.52	0.608	-14
	13	0.774	0.825	-6
	14	0.857	0.902	-5
	15	0.96	1.075	-11
	*16	0.606	0.602	nil
	*17	0.625	0.593	5
	*18	0.6565	0.618	6
	*19	0.613	0.634	-3
	*20	0.64	0.82	-22
	*21	0.64	0.82	-21
	*22	0.53	0.78	-32
	*23	0.58	0.83	-30
$y_2^*$	7	0.93 cm.	2.37 cm.	-61
	8	0.9	2.27	-60
	9	3.6	3.615	nil
	*12	1.1	1.39	-21
	13	1.7	1.91	-11
	14	1.7	2.175	-22
	15	1.8	1.705	6
	*16	0.50	0.6015	-17
	*17	0.95	1.083	-12
	*18	1.36	1.626	-16
	*19	1.65	2.22	-26
	*20	0.65	0.81	-20
	*21	1.1	1.56	-29
	*22	1.55	1.87	-17
	*23	1.95	2.88	-32

TABLE V.

$m/M.$	$l/a.$	Fig.	$t_2/\theta$ % Difference.		$y_2$ % Difference.	
			Helmholtz Theory.	Kaufmann Theory.	Helmholtz Theory.	Kaufmann Theory.
0.267	2	*1	57	nil	-63	11.7
"	2	2	56	2	-63	12.1
"	3	7	23	...	-61	...
"	8/3	8	37	...	-60	...
"	9	6	-16.3	-7.4	-29	-20
1.45	2	*20	-22	...	-20	...
"	"	*21	-21	...	-29	...
"	"	*22	-32	...	-17	...
"	"	*23	-30	...	-32	...
"	20/7	*16	nil	...	-17	...
"	"	*17	5	...	-12	...
"	"	*18	6	...	-16	...
"	"	*19	-3	...	-26	...
1.684	2	3	nil	nil	-2	15.5
"	8/3	9	13	...	nil	...
"	9	4	-4.7	-4.0	4.9	nil
"	26/3	5	-10.0	-10.8	-8.9	-4.0
7.47	9	15	-11	...	6	...
"	10	14	-5	...	-22	...
"	11	13	-6	...	-11	...
9.19	20	*12	-14	...	-21	...

TABLE VI. Description of Figures.

The length ( $l$ ) of the string is 316 cm. for figs. 1-9 and is 100 cm. for figs. 12-23. The linear density of the string is 0.0174 gm. per cm. for figs. 12-15 and is 0.093 gm. per cm. for figs. 1-9 and 16-23.  $\tau$ =duration of impact;  $\theta$ =free period of fundamental tone of string;  $v_0$ =initial velocity of hammer;  $v$ =velocity of rebound of hammer;  $a$ =distance of struck point from nearer bridge.

Fig.	$l/a$ .	$m/M$ .	$m$ .	$\tau/\theta$ .	$v_0$ .	$-v$ .
*1 .....	2	0.269	7.9	0.57	377	262
2 .....	"	"	"	"	338	213
3 .....	"	1.684	49.5	1.0	334	227
4 .....	9	"	"	0.633	361	249
5 .....	26.3	"	"	0.355	375	306
6 .....	9	0.267	7.9	0.243	352	149
7 .....	3	"	"	0.392	391	150
8 .....	8.3	"	"	0.422	358	166
9 .....	"	1.684	49.5	1.0	308	291
*12 .....	20	9.19	16	1.12	348	265
13 .....	11	7.47	13	1.62	350	328
14 .....	10	"	"	1.72	366	314
15 .....	9	"	"	1.87	270	258
*16 .....	20/7	1.45	13.5	1.15	122	106
*17 .....	"	"	"	1.12	222	184
*18 .....	"	"	"	1.14	320	246
*19 .....	"	"	"	1.167	428	327
*20 .....	2	1.45	13.5	1.64	120	120
*21 .....	"	"	"	1.57	230	202
*22 .....	"	"	"	1.45	292	229
*23 .....	"	"	"	1.46	425	275

*Summary of Experimental Results.*—In Part I. of the whole paper it was shown that the first Helmholtz theory is in conflict with experimental evidence.

The experimental results obtained in the second part of the paper, which deals with the second Helmholtz theory, are summarized in Table V. where percentage differences between experiment and theory are classified according to the mass ratio of hammer and string ( $m/M$ ) and striking place ( $l/a$ ). Large differences between experiment and theory occur when a light hammer ( $m/M=0.267$ ) is used, but when the mass ratio of hammer and string is of the order 1.7 experiment and theory agree within the limits of experimental accuracy. In each of the two series figs. 16-19 and 20-23 the initial velocity of the hammer was varied whilst  $m/M$  and  $l/a$  were kept constant. In the complete set of figures the range of  $m/M$  is from 0.267 to 9.19 and of  $l/a$  from 2 to 26.3.

*Plan of the Research.*—The continuation of the work is on the following lines. (I.) Critical examination of the various theories of the struck string with quantitative experiments and comparisons. (II.) Experimental determination of the

pressure-time law of the impact graphically and by an electrical method. (III.) Determination of the velocity-time graph of the struck point by an electromagnetic method and its use in the study of the communication of energy to the system. (IV.) The study of the total energy communicated to the system by the hammer (by the method indicated in Phil. Mag. xlvii. p. 596 (1924)) and its partition among the various partials. (V.) The application of instantaneous photography to the study of the form of the whole string at any instant (*loc. cit.* p. 593).

Throughout the work the influence of at least the following six factors must be studied:—(i.)  $a/l$ ; (ii.)  $m/M$ ; (iii.) tension of the string; (iv.)  $v_0$ ; (v.) dimensions and nature of the hammer-head; and (vi.) vibration of the hammer-shaft.

In addition to previous acknowledgements the writer wishes to thank Dr. H. M. Browning, M.Sc., for occasional help in making experimental adjustments, and Mr. A. H. Franks, B.Sc., for kindly helping to photograph the apparatus.

University College, Nottingham.  
February 1924.

*Note added May 31st, 1924.*

On account of the clearness of the reproduction of the displacement-time curves (figs. 1–23), it seems desirable to comment on some other of their features not mentioned in the paper.

*Momentary separation of hammer and string.*—In each of the figures 1 and 2 a small white patch can be seen at the top of the dark patch between the record of the string's motion and that of the hammer. This shows that during the impact there was complete separation and subsequent contact between hammer and string before the hammer finally quitted the string. This has an important bearing on the determination of the total duration of the impact by electrical methods. These methods, which are by far the most convenient and are widely used to study all cases of impacts between metallic or metal-coated bodies, depend in part on the assumption that the variation in electrical resistance of the contact due to variation in the mechanical forces involved are negligible as compared with the total electrical resistance of the circuit. It is clear that in this particular case such an assumption would be unjustifiable, since the electrical resistance has an infinite value for a portion of the total duration of the impact.



GEORGE.

FIG. 1.

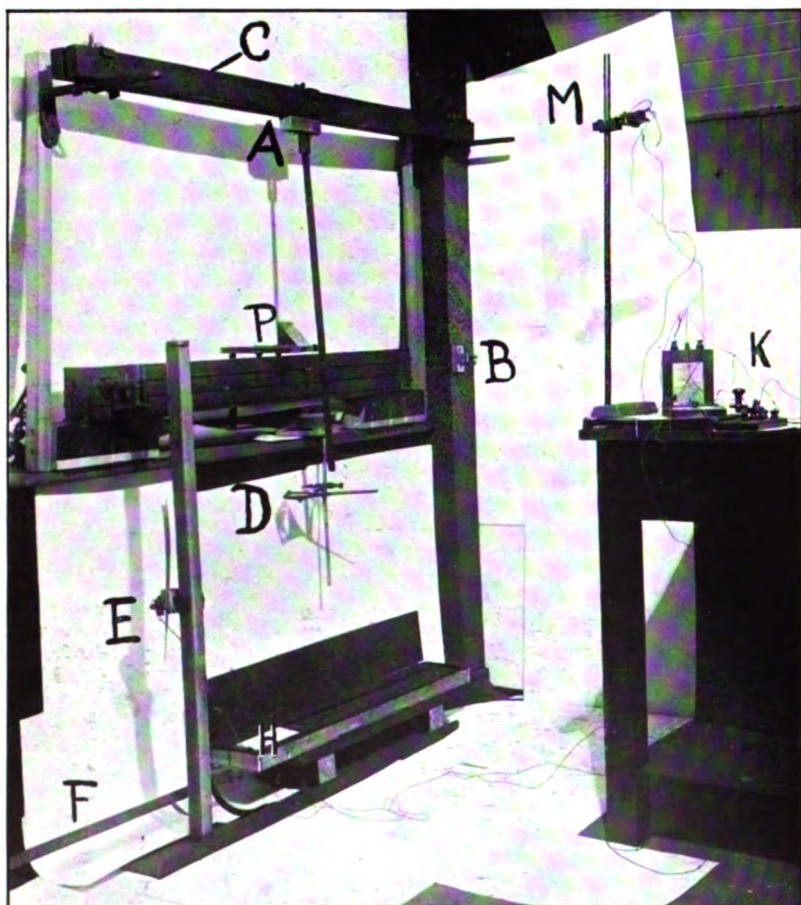
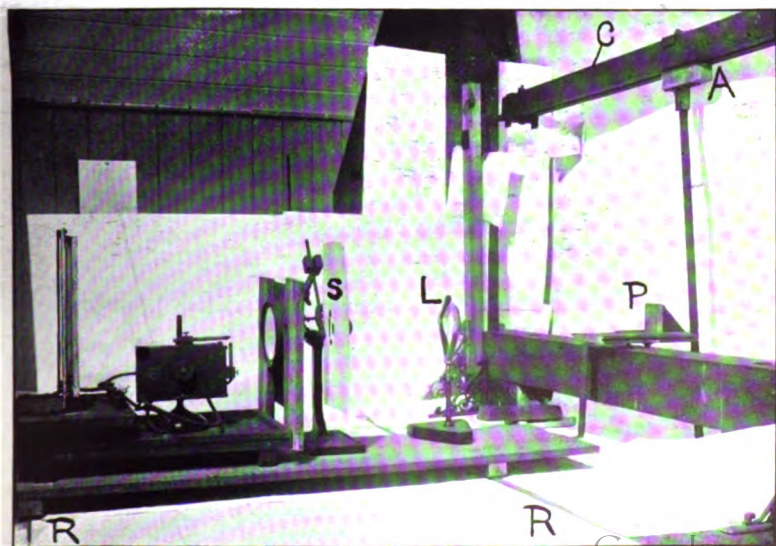


FIG. 2.



FIG. 3.

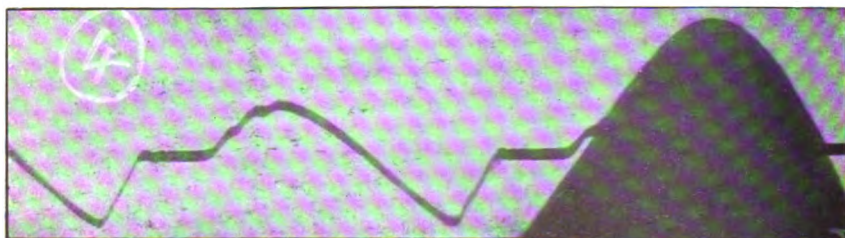
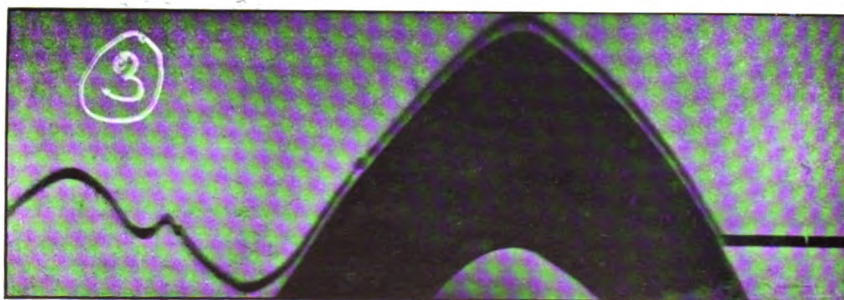
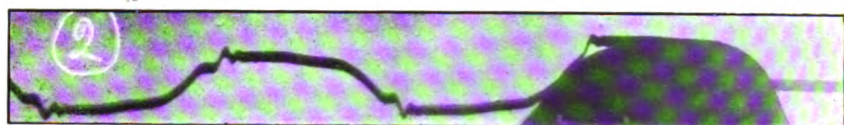
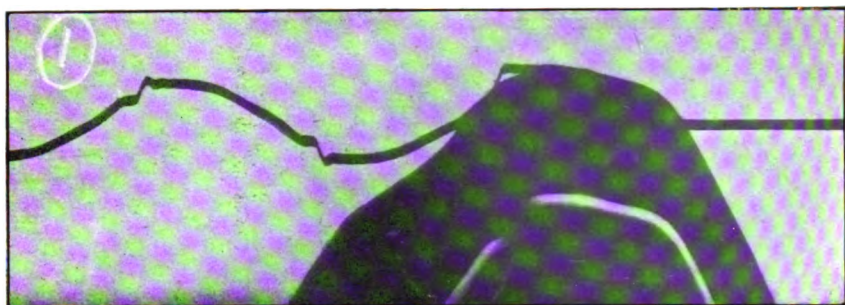


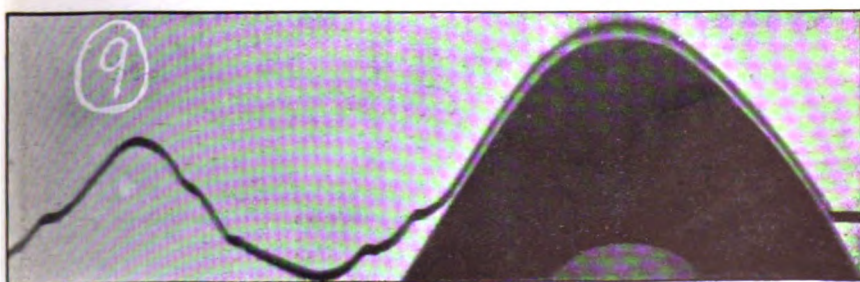
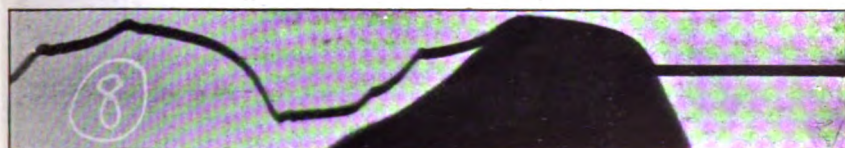
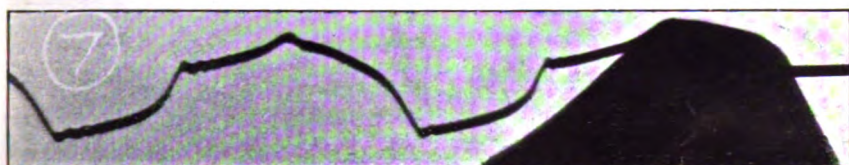
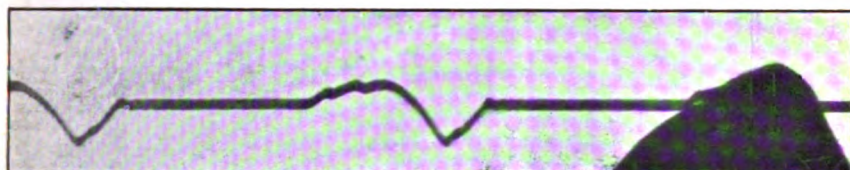
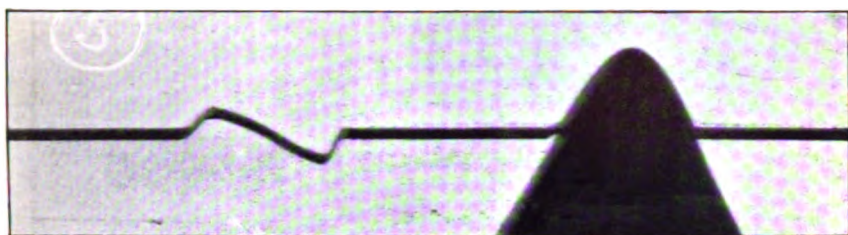






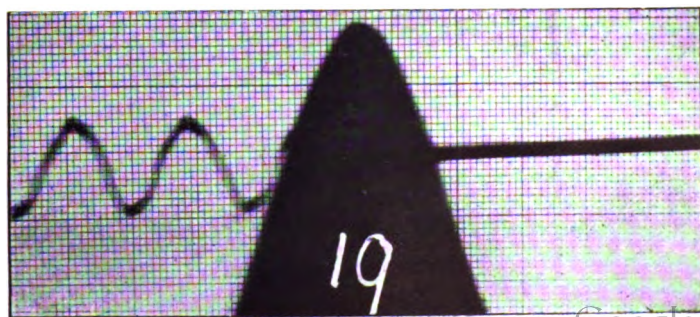
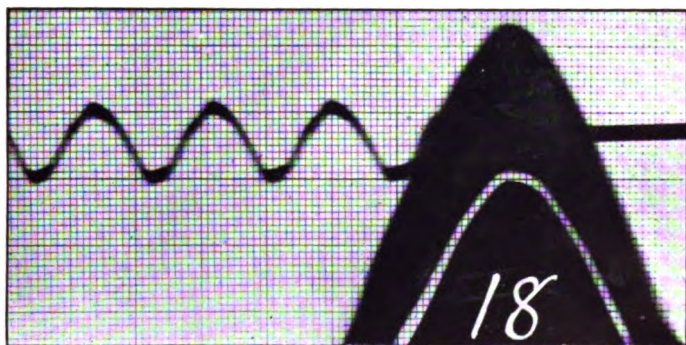
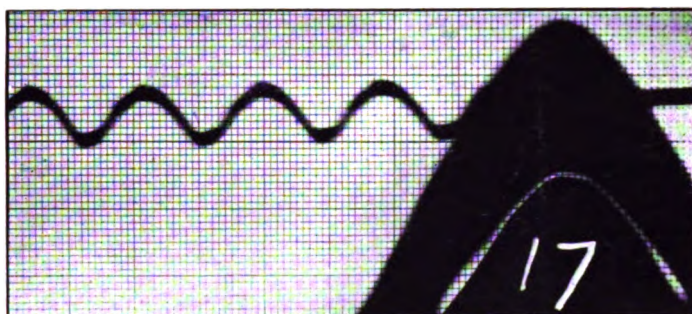
GEORGE.













The present writer has investigated this separation phenomenon by the use of the Duddell Oscillograph. As might be expected, the effect depends on the mass ratio of hammer and string ( $m/M$ ), and on the striking place ( $a/l$ ). Experiments on the influence of other factors are now in progress.

On figs. 3 and 9 a white band about 1 mm. wide can be seen between the record of the string and that of the hammer. This is due to an inexact fixing upon the hammer-head of the strip of foil which cuts off the light. It does not, of course, indicate separation of the hammer and string.

*Distortion of hammer.*—The felt-covered hammer-heads used consist of wedge-shaped pieces of wood round which the felt is tightly wrapped by a machine process. In order to attempt a study of the compression of this felt a small hole was drilled in the narrow end of the wood behind the felt. If now the hammer approach and recede along the line of the slit of light a continuous white line will be seen on the dark patch caused by the hammer's shadow (figs. 17 and 18), and the extent of the compression of the felt can be estimated from the perpendicular distance between the white line and the upper boundary of the dark patch. Before interpreting the result, account must be taken of the produced or already existent curvature of the face of the felt. The break in the white line shown in fig. 1 indicates a slight torsional deflexion of the hammer, the light being cut off until the hammer-head reaches a second hole drilled further from the edge of the felt and a little to the right of the axis of the hammer-head.

Fig. 15 illustrates an alternative method of recording the motion of the metallic type of hammer. A piece of fine wire is stretched across the space between the metal foil of which the hammer is made, so that the wire is parallel to and in the same horizontal plane as the string. The lower line then records the motion of the hammer, whilst the upper line records the motion of the string. This arrangement needs a careful setting of the hammer relative to the image of the slit, otherwise the foil of the hammer may cause a blurred image as in fig. 14.

III. *On Water Waves near the Shore.* By HAROLD JEFFREYS,  
M.A., D.Sc., Fellow and Lecturer of St. John's College,  
Cambridge\*.

**A** GLANCE at a rough sea at a distance from land is enough to show that the waves form no regular pattern, but that as a rule the length of the crest of each wave is comparable with the distance between consecutive waves; thus waves in deep water constitute essentially a three-dimensional phenomenon. This fact appears to be consistent with the hypothesis that such waves are due to turbulence in the wind. For G. I. Taylor has shown that the mean square deviation of the velocity in any direction from its mean value is the same whether the direction be along the wind, across it, or vertical, and that gusts in any direction last about the same time; thus it would be expected that the irregularities set up in the motion of the sea would also have comparable wavelengths in perpendicular horizontal directions.

Near the shore, however, this type of motion breaks down. Waves of the above type may be seen approaching the shore, but when they reach a distance from it, often of the order of fifty metres on a shelving beach, the crests are seen to run together transversely, and to form a series of waves with very long crests approximately parallel to the shore, which then approach the shore and break one by one.

It may be conjectured that this phenomenon is due either to a second-degree effect, due to the height of the waves becoming comparable with the depth of the water, or to the reduction of the depth of the water having a greater magnifying effect on the amplitudes of long-crested waves than on those of short-crested ones. It is shown here that the former alternative is correct.

Taking the former alternative first, let us consider the behaviour of progressive waves in water of uniform depth when the square of the amplitude is retained in the analysis and several types of wave are present. The equations of fluid motion are:—

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -g \frac{\partial \xi}{\partial x}, \quad \dots \quad (1)$$

$$\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -g \frac{\partial \xi}{\partial y}, \quad \dots \quad (2)$$

$$\frac{\partial \xi}{\partial t} = -\frac{\partial}{\partial x} \left\{ (h + \xi)u \right\} - \frac{\partial}{\partial y} \left\{ (h + \xi)v \right\}, \quad \dots \quad (3)$$

\* Communicated by the Author.

where  $u$ ,  $v$  are the horizontal components of velocity in the directions of  $x$  and  $y$  increasing,  $\zeta$  is the vertical displacement of the surface, and  $h$  the depth of the water. If squares of  $u$ ,  $v$ , and  $\zeta$  are neglected it is easily seen that

$$\frac{\partial^2 \zeta}{\partial t^2} = c^2 \left( \frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right), \quad \dots \quad (4)$$

where  $c^2 = gh$  (5). Hence any wave of form

$$\zeta = b \cos \lambda(x - dt) \cos \mu y \quad \dots \quad (6)$$

is an approximate solution, provided

$$\lambda^2 d^2 = c^2 (\lambda^2 + \mu^2) \dots \dots \dots (7)$$

The corresponding values of  $u$  and  $v$  are

$$u = \frac{ghb}{d} \cos \lambda(x - dt) \cos \mu y, \quad \dots \quad (8)$$

$$v = -\frac{gh\mu}{\lambda d} \sin \lambda(x - dt) \sin \mu y. \quad \dots \quad (9)$$

If now two waves of type (6) are present in the motion, and we evaluate the terms of the second degree in (1) (2) and (3), these terms will be found to include some depending on each wave separately and also some product terms containing factors of the form

$$\frac{\cos}{\sin} \left\{ (\lambda_1 \pm \lambda_2)x - (\lambda_1 d_1 \pm \lambda_2 d_2)t \right\} \frac{\cos}{\sin} \left\{ \mu_1 \pm \mu_2 \right\} y. \quad \dots \quad (10)$$

Such terms will satisfy (4) only if

$$(\lambda_1 d_1 \pm \lambda_2 d_2)^2 = c^2 \{ (\lambda_1 \pm \lambda_2)^2 + (\mu_1 \pm \mu_2)^2 \}, \quad \dots \quad (11)$$

or, using (7), if

$$\lambda_1 \lambda_2 d_1 d_2 = c^2 (\lambda_1 \lambda_2 \pm \mu_1 \mu_2) \quad \dots \quad (12)$$

This relation is easily reduced to

$$\frac{\mu_1}{\lambda_1} \pm \frac{\mu_2}{\lambda_2} = 0, \quad \dots \quad (13)$$

in which case the two waves differ only in their horizontal scale; the distances between consecutive crests along and across the direction of propagation are in proportion. For the present purpose such combinations are uninteresting. In general, then, the product terms in (1) (2) and (3) will be such as to give contributions to the solution that are purely



periodic functions of  $x$ ,  $y$ , and  $t$ . They therefore do not imply any change of type in either wave as it advances.

In investigating possible changes in type of each wave it will therefore be enough to consider each wave separately by Airy's method. We have

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \frac{g^2 b^2}{4 \lambda d^2} \sin 2\lambda(x-dt) \{ \mu^2(1 - \cos 2\mu y) - \lambda^2(1 + \cos 2\mu y) \}, \quad (14)$$

$$u \frac{\partial v}{\partial \lambda} + v \frac{dv}{dy} = \frac{\mu g^2 b^2}{4 \lambda^2 d^2} \sin 2\mu y [ \mu^2 \{ 1 - \cos 2\lambda(x-dt) \} - \lambda^2 \{ 1 + \cos 2\lambda(x-dt) \} ], \quad (15)$$

$$\frac{\partial}{\partial x}(u\zeta) + \frac{\partial}{\partial y}(v\zeta) = - \frac{gb^2}{2\lambda d} \sin 2\lambda(x-dt) \{ \lambda^2(1 + \cos 2\mu y) + \mu^2 \cos 2\mu y \}. \quad (16)$$

Except in the case where  $\mu$  is zero, the only terms in these expressions that can lead to non-periodic terms in the solution are those involving both  $2\lambda(x-dt)$  and  $2\mu y$ . We have therefore to solve

$$\frac{\partial u}{\partial t} + g \frac{\partial \zeta}{\partial x} = \frac{\lambda g^2 b^2}{4c^2} \sin 2\lambda(x-dt) \cos 2\mu y, \quad . \quad . \quad . \quad (17)$$

$$\frac{\partial v}{\partial t} + g \frac{\partial \zeta}{\partial y} = \frac{\mu g^2 b^2}{4c^2} \cos 2\lambda(x-dt) \sin 2\mu y, \quad . \quad . \quad . \quad (18)$$

$$\frac{\partial \zeta}{\partial t} + h \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) = \frac{\lambda g b^2}{2c^2} \sin 2\lambda(x-dt) \cos 2\mu y. \quad . \quad . \quad (19)$$

Eliminating  $u$  and  $v$  we find

$$\frac{\partial^2 \zeta}{\partial t^2} - c^2 \left( \frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right) = - \frac{3}{2} \frac{\lambda^2 d^2 g b^2}{c^2} \cos 2\lambda(x-dt) \cos 2\mu y, \quad (20)$$

the relevant particular integral of which is

$$\zeta = \frac{3 \lambda d^2 g b^2}{8 c^4} x \sin 2\lambda(x-dt) \cos 2\mu y. \quad . \quad . \quad (21)$$

Thus the second approximation to the wave form is

$$\zeta = b \cos \lambda(x-dt) \cos \mu y + \frac{3 \lambda d^2 g b^2}{8 c^4} x \sin 2\lambda(x-dt) \cos 2\mu y. \quad (22)$$

The effect of the second term is to make the crests gain on the troughs as the wave advances. The approximation will evidently break down when  $\frac{3}{8} \frac{\lambda d^2 g b}{c^4} x$  becomes comparable with unity. When this is the case the front of the wave has become so steep that the vertical acceleration cannot be neglected in the equation of vertical motion; the crest then curls forward and pours over into the trough, and the wave is destroyed.

If in addition to the above wave a wave with a long crest is present, it will be necessary to include a term  $a \cos \kappa(x - ct)$  in (6), and then a term  $\frac{3}{4} \frac{g \kappa a^2}{c^2} x \sin 2\kappa(x - ct)$  will also have to be included in (22)\*. The factor  $\frac{3}{4}$  arises instead of  $\frac{3}{8}$  on account of the fact that  $\mu$  is here zero, so that the terms independent of  $y$  in (14), (15), and (16) have to be included in the solution. The distance this wave can travel before it collapses is therefore to the distance the former wave can travel in the ratio  $\frac{\lambda l^2 b}{2 \kappa a c^2}$ . Now  $d^2$  is greater than  $c^2$ , but comparable with it so long as  $\mu$  is not large compared with  $\lambda$ , and therefore as a rule this ratio is greater than  $\lambda b / 2 \kappa a$ .

Now we have seen that far from shore the long-crested wave is so small as to be almost unobservable, whereas the short-crested waves are striking. Hence  $b$  is much greater than  $a$ . Also the short-crested waves appear to have the shorter wave-length, so that  $\lambda > \kappa$ . On both grounds, therefore, the critical ratio must be large. Hence as a compound wave advances in shallow water the short-crested constituents tend to annihilate themselves by breaking, while the long-crested wave does not break until all the shorter waves have disappeared. The phenomenon of the predominance of the long-crested wave close to shore is therefore explicable.

If the depth be variable, but the amplitude small compared with the depth, equations (1) (2) and (3) give, when  $u$  and  $v$  are eliminated, the equation

$$\frac{\partial^2 \zeta}{\partial t^2} = g \left\{ \frac{\partial}{\partial x} \left( h \frac{\partial \zeta}{\partial x} \right) + \frac{\partial}{\partial y} \left( h \frac{\partial \zeta}{\partial y} \right) \right\}. \quad (23)$$

Suppose  $h$  to be a function of  $x$  alone, and search for a

\* Lamb, 'Hydrodynamics,' 1906, p. 264.

solution of (23) of the form  $X \cos \gamma t \cos \mu y$ , where  $X$  is a function of  $x$  alone. Then

$$\frac{d}{dx} \left( h \frac{dX}{dx} \right) + (\gamma^2 - gh\mu^2)X = 0. \quad . . . \quad (24)$$

By hypothesis the wave is of harmonic type and is generated in deep water. Hence in deep water  $\gamma^2$  is not less than  $gh\mu^2$ . As the wave passes into shallower water  $\gamma^2$  remains the same but  $h$  diminishes; therefore  $\gamma^2 - gh\mu^2$  is positive. Thus  $X$  is an oscillating function of  $x$ . If we put

$$\int \frac{dx}{h} = \theta \quad . . . . . (25)$$

$$(24) \text{ becomes } \frac{d^2 X}{d\theta^2} + (\gamma^2 - gh\mu^2)hX = 0, \quad . . . . . (26)$$

and provided that  $h$  does not change by a large fraction of itself within a wave-length the amplitude of  $X$  will be proportional to  $\{(\gamma^2 - gh\mu^2)h\}^{-1/4}$ . Thus, subject to the condition that the wave has come from deep water, the amplitude in shallow water will behave nearly like  $h^{-1/4}$  for all waves. Therefore the second alternative offered above, that the long-crested waves are specially magnified in shallow water, does not afford an explanation of the phenomenon.

IV. *On the Delemer and the Lamb Theories of the Struck String.* By W. H. GEORGE, B.Sc., University College, Nottingham\*.

**I**N the study of the struck string the pressure-time law of the impact is of considerable interest, since, if it be completely known, then the intensities of the fundamental tone and partials of the freely vibrating string, and therefore the resulting tone quality, can readily be determined by the well-known analytical method †. Three forms of the pressure-time law have been assumed by Helmholtz, by Delemer, and by Lamb respectively ‡. The present paper is concerned with experimental tests of the two latter theories, the Helmholtz theories having been already considered in two previous

\* Communicated by Prof. E. H. Barton, F.R.S.

† Rayleigh, 'Theory of Sound,' vol. i. §§ 128 & 130.

‡ Helmholtz, 'Sensations of Tone,' App. V.; Delemer, Sci. Abs. A, vol. ix. p. 623 (1906); Lamb, 'Dynamical Theory of Sound,' p. 74 (1910).

papers\*. The treatment is similar to that adopted in the first two papers. Expressions are derived for quantities whose magnitude can be determined from photographically obtained displacement-time curves for the struck point of the string, and the theoretical results are then compared with those found by experiment.

# THEORY.

Notation :—

- $l$  = length of string (in cm.).
- $a$  = distance of struck point from nearer bridge (in cm.).
- $y$  = variable displacement of struck point reckoned positive in the direction of the approaching hammer (in cm.).
- $y_1$  = displacement of struck point at the instant of separation of hammer and string (in cm.).
- $y_2$  = maximum displacement of struck point (in cm.).
- $r$  = distance between string and axis of rotation of hammer (in cm.).
- $\theta$  = free period of fundamental tone of string (in sec.).
- $\tau$  = duration of impact (in sec.).
- $t$  = variable time reckoned from the instant of the beginning of the impact (in sec.).
- $t_2$  = time taken for  $y$  to reach its maximum value (in sec.).
- $v_0$  = initial velocity of hammer (in cm. per sec.).
- $v$  = velocity of hammer at instant of separation of hammer and string (in cm. per sec.).
- $\mu$  = linear density of string (in gm. per cm.).
- $m$  = mass of hammer (see following note).
- $M$  = mass of string =  $\mu l$  (in gm.).

The actual hammer under consideration may be regarded as a compound pendulum. By the term "*mass of hammer*" is meant the mass in gm. of a particle equimomental with the hammer and distant  $r$  from the axis of rotation of the pendulum. The motion is assumed to take place in one plane passing through the string.

*Delemer Theory.*—The pressure of the hammer is assumed to be constant during the time of contact. We may therefore write for the force on the hammer

$$m \frac{d^2 y}{dt^2} = K. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$(0 < t < \tau)$

\* Phil. Mag. xlvii. pp. 591–602 (1924), and *suprà*, p. 34. These will be referred to as the first and second papers respectively.

Hence

$$\int_{v_0}^{\frac{dy}{dt}} d\left(\frac{dy}{dt}\right) = \frac{K}{m} \int_0^t dt,$$

giving

$$\frac{dy}{dt} = v_0 + \frac{K}{m} t. \quad (2)$$

Since the quantity  $K$  is not readily determined by experiment, we may eliminate it from the equations by introducing the new quantity ( $v$ ), which is the velocity of rebound of the hammer (see first paper, p. 596). By putting  $t = \tau$  in equation (2) we have:—

$$v = v_0 + (K\tau)/m \quad \text{or} \quad K = m(v - v_0)/\tau.$$

Hence equation (2) may be rewritten thus:—

$$\frac{dy}{dt} = v_0 + (v - v_0) \frac{t}{\tau}. \quad (2a)$$

( $0 < t < \tau$ )

Integrating again and putting in the condition that  $y = 0$  when  $t = 0$ , we have

$$y = v_0 t - \frac{1}{2} (v_0 - v) \frac{t^2}{\tau}. \quad (3)$$

( $0 < t < \tau$ )

By putting  $t = \tau$  in this equation, we see that the displacement of the struck point at the instant of separation of hammer and string is given by

$$y_1 = \frac{1}{2} (v_0 + v) \tau. \quad (4)$$

This is identical with the expression for  $y_1$  derived from the second Helmholtz theory (eqn. (5) of the first paper).

The time ( $t_2$ ) taken for  $y$  to reach its maximum value ( $y_2$ ) is obtained from equation (2a), whence

$$t_2 = \frac{\tau v_0}{v_0 - v}. \quad (5)$$

Hence

$$y_2 = \frac{1}{2} \frac{\tau v_0^2}{v_0 - v}. \quad (6)$$

*Lamb Theory.*—In this case we may write for the force on the hammer:—

$$m \frac{d^2 y}{dt^2} = - \frac{2}{\pi} \cdot \frac{I \tau}{t^2 + \tau^2}, \quad (7)$$

where  $I$  represents the time-integral of the force from

$t = -\infty$  to  $t = +\infty$ . Proceeding as before, we have:—

$$\int_{v_0}^{\frac{dy}{dt}} d\left(\frac{dy}{dt}\right) = \frac{-2I}{\pi m} \int_0^t \frac{\tau dt}{(t^2 + \tau^2)}$$

or

$$\frac{dy}{dt} = v_0 - \frac{2I}{\pi m} \tan^{-1} \frac{t}{\tau}, \quad \dots \dots \dots (8)$$

since  $t/\tau$  is never greater than unity. To eliminate the quantity  $I$ , we put  $t = \tau$  in equation (8), whence

$$v = v_0 - I/(2m) \quad \text{or} \quad I = 2m(v_0 - v).$$

Hence equation (8) may be re-written:—

$$\frac{dy}{dt} = v_0 - \frac{4}{\pi} (v_0 - v) \left( \tan^{-1} \frac{t}{\tau} \right) \quad \dots \dots (8a)$$

$(0 < t < \tau)$

Integrating again with respect to time and putting in the condition that  $y = 0$  when  $t = 0$ , we have

$$y = v_0 t - \frac{4}{\pi} (v_0 - v) \left[ t \tan^{-1} \frac{t}{\tau} - \frac{\tau}{2} \log_e \left( 1 + \frac{t^2}{\tau^2} \right) \right]. \quad (9)$$

Putting  $t = \tau$  in this equation, we have

$$y_1 = \tau \left\{ v_0 - (v_0 - v) \left[ 1 - \frac{2}{\pi} \log_e 2 \right] \right\} \quad \dots \dots (10)$$

Putting  $dy/dt = 0$  in equation (8a), we find

$$t_2 = \tau \tan \left[ \frac{\pi v_0}{4(v_0 - v)} \right] \quad \dots \dots \dots (11)$$

Hence the maximum displacement ( $y_2$ ) of the struck point is given by:—

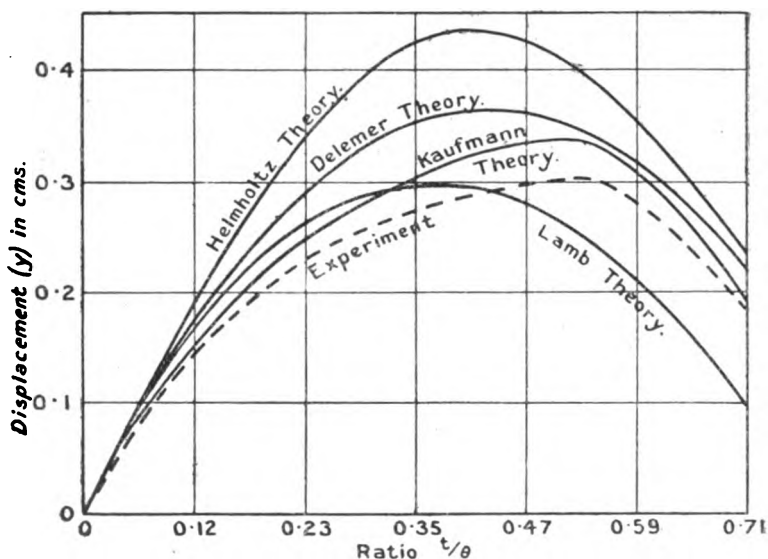
$$y_2 = \frac{-4\tau(v_0 - v)}{\pi} \log_e \cos \left\{ \frac{\pi v_0}{4(v_0 - v)} \right\} \quad \dots \dots (12)$$

The corresponding expressions derived from the Helmholtz and the Kaufmann theories were given in the first paper.

## EXPERIMENTAL RESULTS.

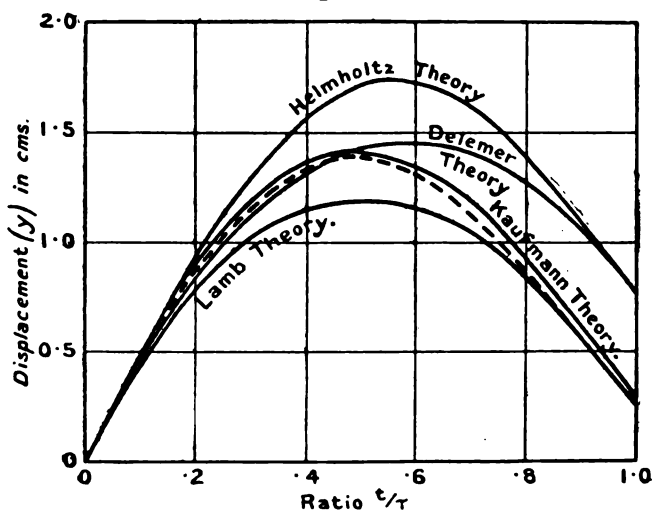
The measurements required in order to compare experiment and theory were made upon the displacement-time curves reproduced in Pls. II. & III. of the second paper.

Fig. 1.



Comparison of theoretical displacement-time curves for the struck point with the experimental curve.  $M=4.8$ ;  $m=4.4$ ;  $\theta=1/128$ ;  $\tau/\theta=0.74$ ;  $v_0=215$ ;  $v=-149$ ;  $l/a=2$ .

Fig. 2.



Comparison of theoretical displacement-time curves for the struck point with the experimental curve.  $M=29.4$ ;  $m=49.5$ ;  $m_0=50.6$ ;  $\theta=1/46.1$ ;  $\tau/\theta=0.633$ ;  $v_0=361$ ;  $v=-249$ ;  $l/a=9$ .

TABLE I.

Fig.	$t_2/\theta$ by experiment.	$t_2/\theta$ on Delemer Theory.	$t_2/\theta$ on Lamb Theory.	% Difference on Delemer Theory.	% Difference on Lamb Theory.
1*	0.50	0.336	0.285	49	75
2	0.51	0.350	0.298	46	71
3	0.56	0.596	0.504	- 5	12
4	0.31	0.375	0.317	-19	- 4
5	0.17	0.195	0.163	-13	4
6	0.12	0.170	0.150	-32	-23
7	0.31	0.283	0.249	10	25
8	0.36	0.289	0.279	24	28
9	0.57	0.514	0.427	12	35
12*	0.52	0.636	0.537	-18	- 3
13	0.77	0.836	0.696	- 7	11
14	0.86	0.926	0.774	- 7	11
15	0.96	0.955	0.795	nil	21
16*	0.61	0.615	0.516	- 1	17
17*	0.62	0.613	0.513	2	22
18*	0.66	0.643	0.542	2	21
19*	0.61	0.662	0.558	- 7	10
20*	0.64	0.820	0.678	-22	- 6
21*	0.64	0.836	0.697	-23	- 8
22*	0.53	0.813	0.682	-35	-22
23*	0.58	0.887	0.752	-35	-23

TABLE II.

Fig.	$y_2$ by experiment.	$y_2$ on Delemer Theory.	$y_2$ on Lamb Theory.	% Difference on Delemer Theory.	% Difference on Lamb Theory.
1*	1.0	2.26	1.84	-56	-46
2	0.9	2.10	1.72	-57	-48
3	4.1	3.53	3.46	16	18
4	2.36	3.15	1.99	-25	19
5	1.5	1.34	1.30	12	16
6	0.7	1.12	0.93	-38	-25
7	0.93	2.03	1.69	-54	-45
8	0.9	1.89	1.88	-52	-52
9	3.6	2.87	2.32	25	55
12*	1.1	1.15	0.94	- 4	17
13	1.7	1.52	1.23	12	38
14	1.7	1.76	1.35	- 3	26
15	1.8	1.34	1.08	34	66
16*	0.5	0.49	0.40	2	26
17*	0.95	0.88	0.72	8	32
18*	1.36	1.34	1.09	1	25
19*	1.65	1.84	1.50	-10	10
20*	0.65	0.64	0.52	2	26
21*	1.1	1.25	1.02	-12	8
22*	1.55	1.55	1.25	nil	24
23*	1.95	2.45	2.00	- 2	2



TABLE III.

$m$ $\bar{M}$	$\frac{l}{a}$	Fig.	$t_3/\theta$ % Differences.				$y_3$ % Differences.			
			Helmholtz Theory.	Kaufmann Theory.	Delemer Theory.	Lamb Theory.	Helmholtz Theory.	Kaufmann Theory.	Delemer Theory.	Lamb Theory.
495.0	2	1*	57	Nil	49	75	-63	12	-56	-46
	2	2	56	2	46	71	-63	12	-57	-48
	2	7	23	...	10	25	-61	...	-54	-45
	8/3	8	37	...	24	28	-60	...	-52	-52
	9	6	-16	-7	-32	-23	-29	-20	-38	-25
57.1	2	20*	-22	...	-22	-6	-20	...	2	26
	"	21*	-21	...	-23	-8	-29	...	-12	8
	"	22*	-32	...	-35	-23	-17	...	Nil	24
	"	23*	-30	...	-35	-23	-32	...	-2	2
	20/7	16*	Nil	...	-1	17	-17	...	2	26
	"	17*	5	...	2	22	-12	...	8	32
	"	18*	6	...	2	21	-16	...	1	25
	"	19*	-3	...	-7	10	-26	...	-10	10
	2	3	Nil	Nil	-5	12	-2	16	16	18
	8/3	9	13	...	12	35	Nil	...	25	55
169.1	9	4	-5	-4	-19	-4	5	Nil	-25	19
	26.3	5	-10	-11	-13	4	-9	-4	12	16
	9	15	-11	...	Nil	21	6	...	34	66
	10	14	-5	...	-7	11	-22	...	-3	26
	11	13	-6	...	-7	11	-11	...	12	38
9.19	20	12*	-14	...	-18	-3	-21	...	-4	17
Mean % Difference .....			1	...	-4	13	-24	...	-10	9
Mean % Difference for figs. 1-6			14	-3	4	22	-26	3	-25	-11

There also will be found details of the apparatus used and the necessary data for the calculations. In figs. 1 and 2 of the present paper typical experimental displacement-time curves of the struck point are compared with the curves predicted by four different theories. The experimental curve in fig. 1, which refers to a string struck at its mid-point, is taken from Kaufmann's paper (p. 693), whilst that in fig. 2, which refers to a string struck near one end, is taken from the curve reproduced in Pl. II. fig. 4 of the second paper. In each figure the experimental curve is shown dotted.

In each of Tables I. and II. quantities determined by experiment are compared with those predicted by the Delemer and the Lamb theories. The values of  $y_2$  given in Table II. are the magnified values of the actual displacement of the struck point of the string, but the displacements shown in the graphs of fig. 2 represent the actual displacements of the struck point. This explains the apparent discrepancy between the value of  $y_2$  given in the table and that shown on the graph. By the term "*percentage difference*" is meant throughout the paper  $[100(\text{Expmtal. Value} - \text{Theo. Value})] \div (\text{Theo. Value})$ . An asterisk denotes the use of a felt-covered hammer-head. The absence of an asterisk denotes the use of a wedge-shaped metallic hammer-head.

The experimental results obtained in this and the second paper are summarized in Table III., where percentage differences between experiment and theory are classified according to the mass ratio of hammer and string ( $m/M$ ) and striking place ( $l/a$ ), these being the two most important factors. In each of the two series, 16-19 and 20-23, the initial velocity ( $v_0$ ) of the hammer was varied, whilst  $m/M$  and  $l/a$  were kept constant. In the complete set of figures the range of  $m/M$  is 0.267-9.19 and of  $l/a$  is 2-26.3.

Acknowledgments and the plan of the continuation of the research were given at the end of the second paper.

University College,  
Nottingham,  
March 1924.

V. *Ionization, Excitation, and Dissociation of Gases.* By  
A. LL. HUGHES, *Wayman Crow Professor of Physics,*  
*Washington University, Saint Louis* †.

THE purpose of this communication is to call attention to a number of researches recently published on effects involving ionization, excitation, and dissociation in gases, to point out apparent difficulties in correlation, and to draw certain tentative conclusions. The investigations to be referred to deal almost entirely with hydrogen. The ionizing and radiating potentials of hydrogen have been studied by numerous physicists. Among the published results, perhaps those of Franck, Knipping and Kruger ‡ stand out as being most directly accounted for by theory. According to these investigators, hydrogen has the following critical potentials:—

I. P.	R. P.	Origin.
11.5	—	Molecular ionization ( $\text{H}_2^+$ ).
—	13.6	Dissociation and excitation ( $\text{H}$ and $\text{H}^*$ ). ( $3.5 + 10.2 = 13.7$ volts.)
17.1	—	Dissociation and ionization ( $\text{H}$ and $\text{H}^+$ ). ( $3.5 + 13.5 = 17.0$ volts.)
30.4	—	Dissociation and ionization of both atoms ( $\text{H}^+$ and $\text{H}^+$ ). ( $3.5 + 13.5 + 13.5 = 30.5$ volts.)

The symbol  $\text{H}^*$  may conveniently denote an excited atom.

Similar results have been obtained by Olmstead § and by Horton and Davies ||, except that the corresponding voltages are about a volt lower. Horton and Davies, however, do not find ionization near 11.5 volts. In addition to the critical potentials listed by Franck, Kruger and Knipping, they find molecular ionization ( $\text{H}_2^+$ ) at 22.8 volts, and dissociation plus atomic ionization plus atomic excitation ( $\text{H}^+$  and  $\text{H}^*$ ) at 26.1 volts. (One might have expected them to find a critical potential at 22.8 volts corresponding to  $\text{H}^*$  and  $\text{H}^*$ . However, they find the critical potential at 22.8 volts to be an ionizing potential for the molecule.)

† Communicated by the Author.

‡ Franck, Knipping & Kruger, *Verh. d. Deutsch Phys. Ges.* **xxi.** • p. 728 (1919).

§ Olmstead, *Phys. Rev.* **xix.** p. 189 (1922).

|| Horton & Davies, *Phil. Mag.* **xlvi.** p. 872 (1923).

Thus, those critical potentials involving dissociation are explained quantitatively in terms of Bohr's theoretical values for the ionizing and radiating potentials of the atom, together with a value for the energy required to dissociate the hydrogen molecule. The value which suits Franck, Knipping and Kruger's results is 3.5 volts, while Olmstead's results and those of Horton and Davies require a value about 2.4 volts.

In all these investigations, the interpretation of any particular critical potential as a molecular effect, or as an atomic effect accompanied by dissociation, is not the result of direct experimental demonstration, but is inferred from the suggestions of theory and the hints given by the spectroscopic evidence. The application of positive-ray analysis by Smyth\* to ionizing potential experiments introduced a direct experimental demonstration of the nature of the positive ions produced at different ionizing potentials. Smyth's results on hydrogen do not bear out the conjectures of the foregoing authors as to the nature of the ionizing potential at about 16 to 17 volts. Smyth found that  $H_2^+$  appeared alone at this potential without a trace of  $H^+$ . Atomic ions ( $H^+$ ) first appeared at 20.7 volts. Thus the previous interpretation of the process started at the 16-17 volts ionizing potential is incorrect. Smyth's work also shows that even with energies of impact running as high as 600 volts, the proportion of  $H^+$  ions to  $H_2^+$  ions is exceedingly small. No definite statement is made, but fig. 2 in his paper† suggests that  $H^+/H_2^+$ , i.e. the ratio of the number of atomic ions to the number of molecular ions, is considerably less than 1 in 20; perhaps it is as small as 1 in 50. Fig. 3 in the same paper suggests that at 22 volts  $H^+/H_2^+$  is less than 1 in 200. For nitrogen the ionizing potential at 16.9 volts is an ionization of the molecule, while atomic ions do not appear until 27.0 volts. Also the ratio  $N^+/N_2^+$  is less than 15 per cent. up to 370 volts impact energy. Smyth found that in hydrogen the number of atomic ions relative to the number of molecular ions increased very much with the pressure, showing that atomic ions could be obtained plentifully as a secondary process (e.g. a collision between a positive molecular ion and a neutral molecule). However, when the pressure was so low that the secondary processes were negligible, then the yield of atomic positive ions as compared with the yield of molecular ions was exceedingly small, so that in

\* Smyth, Proc. Roy. Soc. cv. p. 116 (1923); civ. p. 121 (1923).

† Smyth, Proc. Roy. Soc. cv. p. 116 (1923).

the great majority of cases the direct result of a collision between an electron and a molecule is the formation of molecular ion, and not the dissociation of a molecule accompanied by the formation of an atomic ion. Similar results were obtained by Dempster\* also by a positive-ray analysis method.

The writer† carried out an investigation two years ago on the dissociation of hydrogen and nitrogen by electron impacts as a function of the energy of impact. The experimental arrangement was a very simple one. An oxide-coated filament was mounted axially in a glass tube lined with nickel gauze, so that electrons could be accelerated from the filament to the gauze by an applied potential. Hydrogen or nitrogen was introduced at a pressure sufficiently low to ensure that an electron would rarely make two collisions in its journey from the filament to the gauze. Provided that the accelerating voltage was above 13 volts for hydrogen and above 17 volts for nitrogen, there was a progressive decrease in pressure as the electron current passed across the tube. Following Langmuir's extensive work on dissociation of hydrogen by heat, this decrease in pressure was interpreted as due to the condensation of atoms produced by the dissociating collisions on the walls of the tube, which was immersed in liquid air. From the rate of disappearance of the gas, the electron current, the dimensions of the tube, etc., the number of collisions resulting in dissociation could be calculated for each accelerating voltage. The curves for hydrogen and nitrogen are shown in figs. 1 and 2. (The ordinates in these curves have been recomputed on the basis of recent values for the collision frequency of electrons in hydrogen and nitrogen, viz. 12·24 and 23·53, in place of the older values assumed in the paper referred to.) It will be seen that the number of collisions resulting in dissociation in hydrogen is as much as 1 in 3 at the most favourable energy of impact (about 100 volts). In view of Smyth's and Dempster's observations that atomic ions can be obtained plentifully as a secondary process, it is necessary to make sure that the dissociations measured in this research are due directly to the primary electron impact, and not to any secondary process. If the dissociations observed were the direct and immediate result of a collision between a molecule and an electron, then the yield of dissociating collisions in terms

\* Dempster, *Phil. Mag.* xxxi. p. 434 (1916); *Phys. Rev.* viii. p. 651 (1916).

† Hughes, *Phil. Mag.* xli. p. 778 (1921).

of the total number of collisions should be a constant independent of the pressure. If, on the other hand, the dissociation were the result of a secondary action, such as a collision between a normal molecule and an ionized molecule, then the yield of dissociating collisions in terms

Fig. 1.

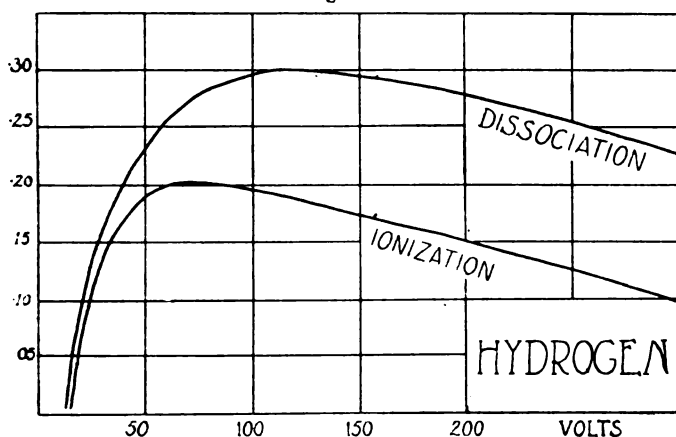
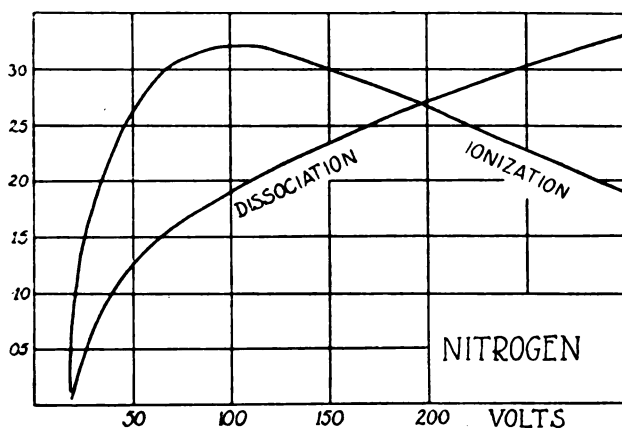


Fig. 2.



of the total number of collisions between electrons and molecules should increase directly as the pressure. In the experiments referred to, it was found that the fraction of collisions resulting in dissociation was practically constant and independent of the pressure. (In fact, the tendency was such as to suggest that the *lower* the pressure, the

greater the yield of dissociating encounters. This, however, could be explained by the fact that the glass takes up atoms less and less readily as it gets more and more covered by atoms.) It seems clear, therefore, that what was measured in these experiments is the fraction of collisions resulting in dissociation as a direct effect of an encounter between an electron and a molecule. Again, the dissociation effect starts at 13 volts for hydrogen and 17 volts for nitrogen. As both these are recognizable as critical potentials for these gases, and as no dissociation of hydrogen occurs at 3.5 volts (the value given by Langmuir for the amount of energy necessary to dissociate a hydrogen molecule), it is natural to conclude that dissociation by electron impact cannot occur alone. Dissociation by electron impact is to be regarded as always accompanied by simultaneous ionization, or by simultaneous excitation of one (or both) atoms.

The diagrams also contain curves (named "ionization") showing the fraction of collisions resulting in the formation of ions (atomic and molecular both count in) at different energies of impact of electrons. (This work was done by the author and Dr. Klein †.) There is a great similarity between the dissociation and ionization curves in the case of hydrogen, but none in the case of nitrogen.

We are now in a position to compare the writer's results on dissociation with those of Smyth on the nature of the positive ions. In the case of hydrogen, at the most favourable energy of impact, fig. 1 shows that about one collision in every three results in dissociation. If this dissociation is accompanied by ionization, then the yield of atomic ions cannot be less than half of the yield of molecular ions, which presupposes that the two remaining non-dissociating collisions both result in molecular ions. However, Smyth's experiments show that the number of atomic ions produced is only a very small fraction of the number of molecular ions. Hence it seems necessary to conclude that the dissociation in my experiments was not accompanied by atomic ionization. The possible direct effects of a collision between an electron and a molecule may be enumerated as follows:—

- (1) Ionization without dissociation. ( $H_2^+$ ).
- (2) Ionization with dissociation. . ( $H$  and  $H^+$ ).
- (3) Excitation without dissociation. ( $H_2^*$ ).
- (4) Excitation with dissociation. . ( $H$  and  $H^*$ ).

† Hughes & Klein, Phys. Rev. (in print).

In process (1) we obtain a positive molecular ion, while in (2) we obtain an atomic ion. In (3) we have an electron removed to one of the outer orbits of the molecule, so that in falling back to its normal orbit the molecule gives out its characteristic band spectrum. In (4) the atom finds itself with an electron in one of the outer orbits, which condition enables it to emit its line spectrum. According to this way of viewing the effects of a collision between an electron and a molecule, a dissociating collision need not necessarily be accompanied by ionization; it may equally well result in the production of one (or two) excited atoms. Smyth's results, together with those of the writer on the dissociation of hydrogen, suggest that in this gas (*a*) collision can frequently result in dissociation; (*b*) it seldom results in the formation of an atomic ion, and therefore, according to the scheme outlined above, (*c*) the dissociation must always be accompanied by excitation of one (or both) atoms. In view of Smyth's conclusions, the ionization curve of fig. 1 must be interpreted as the number of molecular ions formed at different energies of impact, the number of atomic ions being negligible. Had Smyth's results not been available, however, the similarity in the shapes of the ionization curve and the dissociation curve in fig. 1 would have naturally been taken to indicate that the ions obtained were atomic ions accompanying dissociation, and not molecular ions.

The writer and Mr. Lowe carried out an investigation on the distribution of intensity in the spectrum of hydrogen as a function of the energy of impact between the electrons and molecules. This research\*, together with another on helium†, was undertaken to find out what variations in the distribution of intensity were produced as one, and only one, variable, viz. the energy of impact of the electron, was changed. This is clearly the most fundamental variable in the excitation of the spectrum of any gas, as it is the one whose effect would persist at infinitely low pressure, when the mutual effect of atoms causing the pressure-effect would no longer be appreciable. It would also persist at infinitely small current densities, when the presence of charges in the gas in the form of electrons or ions would no longer appreciably influence the emission of radiation from any excited atom. The energy of impact of the electron on the atom is therefore to be regarded as the most fundamental variable in studies of energy distribution in the spectrum.

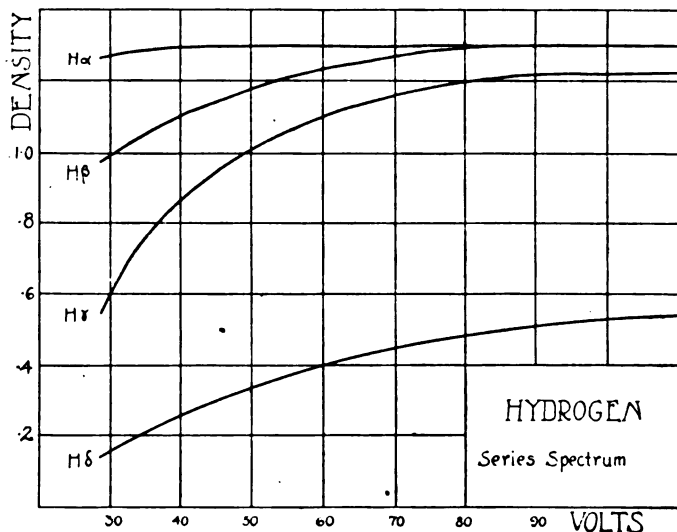
\* Hughes & Lowe, *Phys. Rev.* xxi. p. 292 (1923).

† Hughes & Lowe, *Proc. Roy. Soc. civ.* p. 480 (1923).



In the experiments referred to, the electrons were accelerated from an oxide-coated filament through a grid into a field-free space between the grid and a "plate" at the same potential. The "plate" was so shaped that it almost completely enclosed the region in which the spectrum was excited. The pressure was sufficiently low, so that any ions produced would reach the metallic boundaries of the region and be discharged far oftener than they would recombine with electrons. Consequently we may infer that the production of the spectrum under these particular experimental conditions should be attributed almost entirely to excited, or partially ionized, molecules or atoms, and hardly at all to recombination between ions and electrons. This is a considerable simplification in the conditions of excitation of

Fig. 3.



the spectrum. Under these circumstances it is found that the intensities of the series lines increased asymptotically to a limit as the energy of impact of the electron is increased, and, moreover, the increase is greater the higher the term number of the line (fig. 3). On the other hand the intensities of the secondary lines associated with the molecule fall off rapidly with increasing energy of impact. These results would indicate that process (4) increases, while process (3) decreases, as the energy of impact of the electron is increased. It is unfortunate that the hydrogen spectrum was not studied above 100 volts energy of impact. However, up to this point there is a rough parallelism between

the dissociation curve for hydrogen and the curve for the excitation of the series lines. A close parallelism is not to be expected, for each series line is to be associated with a very special process, while the dissociation curve, on our view, would correspond to the aggregate of all such processes. Thus a dissociation of the hydrogen molecule into two atoms, in one or both of which the electron is shifted to the 5th orbit and thence falls back directly to the 2nd orbit (since  $H\gamma$  is denoted by  $R(1/2^2 - 1/5^2)$  in the Bohr theory), would be registered by the  $H\gamma$  curve in fig. 3. The dissociation curve, on the other hand, would correspond to the sum of all possible transitions in the atoms after dissociation.

These spectroscopic results support, qualitatively at any rate, the view that process (4) occurs frequently as a result of an encounter between an electron and a molecule of hydrogen.

Whiddington\* has recently published a short paper on the excitation of the hydrogen spectrum. He points out that in the laboratory one seldom gets more than four lines of the Balmer series, while in the stars over thirty lines have been found. He suggests that in the stars (1) the pressure is probably extremely low, and (2) the gas may be bombarded continuously and intensely by electrons from the interior. The first condition favours the production of many lines by reason of the comparative isolation of the radiating atom and the consequent realization of its possible outer orbits; the second condition because of the greater opportunity of combination of the positive hydrogen ion with an electron rather than with a negative ion. He describes an experiment in which he used a tube provided with an incandescent tungsten wire cathode to provide sufficient electrons at all degrees of exhaustion. He obtained only the first four lines when his hydrogen was at 1 mm. pressure, but when he reduced the pressure to below .001 mm., about twenty lines of the series were identified. The results of the writer and Mr. Lowe suggest an alternative explanation. According to fig. 3, when the electrons with low energies collide with molecules, the lines of higher term number are relatively much weaker than when the impact energy is high. In Whiddington's experiments at 1 mm. pressure the mean free path of the electron is only .082 cm., and consequently it seems extremely unlikely that the electrons could pick up nearly as much energy before making collisions under these conditions as when the pressure was a thousand times

\* Whiddington, *Phil. Mag.* xlv. p. 605 (1923).

less. Hence it might well be that the effect observed by Whiddington is to be attributed to differences in impact energy rather than to mere change in pressure irrespective of impact energy. Whiddington remarks that increasing the current (in the experiments at 1 mm. pressure) failed to change appreciably the relative intensities of the lines. This would follow our view, since the average energy of impact would not be altered if the potential across the tube remained constant. (There is, of course, a difference between Whiddington's experiments and ours, in that in our work the emission of radiation is attributed to excitation alone, while in his work recombination occurs in addition to excitation.)

In a recent letter to 'Nature'\*, Horton and Davies, in discussing certain features of Lemon's work, consider that certain changes in the appearance of the hydrogen spectrum are due to changes in the energy of the bombarding electrons, and not to changes in the intensity of the electron current apart from any changes in impact energy. This view is in agreement with the view taken by the writer and Mr. Lowe in their recent investigations on the distribution of intensities in the spectrum of hydrogen and helium, that the fundamental variable is the energy of impact of the electron on the molecule.

### *Summary.*

1. A discussion of Smyth's investigation of the nature of the positive ion (*i. e.* whether atomic or molecular) following ionization by electron impact, and of the writer's investigation on the dissociation of hydrogen by electron impacts, points to the conclusion that dissociation of hydrogen molecules by electron impacts is accompanied much more often by excitation of the atoms than by ionization.

2. That dissociation of hydrogen molecules is frequently accompanied by excitation of the atoms receives strong support from an investigation of the distribution of energy in the spectrum of hydrogen as a function of the energy of impact of the electron.

3. Attention is drawn to the view that the fundamentally important variable in determining the character of a spectrum and, in particular, the distribution of intensity in it, is the energy of impact of the electron on the molecule.

Washington University,  
Saint Louis, U.S.A.,  
March 22, 1924.

\* Horton & Davies, 'Nature,' p. 273 (Feb. 23, 1924).

VI. *On the Equation of Long Waves in Canals of Varying Sections.* By N. SEN, Ph.D.\*

MANY solutions of the equation of propagation of long waves in canals of varying sections have been obtained suitable for special forms of sections. The earliest investigator on the subject was Green †, who showed that in the case of progressive waves in a canal with slowly varying sections the elevation of water is inversely proportional to the square root of the breadth and to the fourth root of the average depth at a section. Soluble cases for different types of sections have been investigated by many other writers ‡. In the present paper some special solutions, analogous to those corresponding to the motion of progressive waves, have been discussed, and the laws of variations of depth and breadth for which such types of motion can exist have been deduced, and the possibility of a wider applicability of Green's law has been indicated. It will, in fact, be found that the function  $b^{1/2}h^{1/4}$  ( $b$ =breadth,  $h$ =average depth of a section) plays a very important part in the theory. The subject has not, in reality, been dealt with here as a problem in wave-motion with considerations of the proper boundary conditions, but the investigation has been limited to the discussion of certain types of solutions of the general equation with suitable values for the two arbitrary functions which correspond to the breadth and depth at any section of the canal. A similar and detailed study has been made by Wedderburn § in the case where there is only one arbitrary function in the equation, and his results correspond to motions in canals of constant breadth. We shall retain here both the arbitrary functions  $b$  and  $h$ . Any novelty in the types of solutions discussed here is not claimed, but some simple formulæ have been obtained which automatically adjust the two arbitrary functions in such a way as to lead directly to the solutions under consideration.

If  $\eta$  be the elevation of liquid,  $b$  and  $S$  the breadth

\* Communicated by the Author.

† Green's Mathematical Papers, p. 225.

‡ Chrystal, "Some Results in the Mathematical Theory of Seiches," Proc. R. Soc. Edin. xxv. p. 328 (1904); Lamb, 'Hydrodynamics,' 3rd edition, p. 259.

§ J. Wedderburn, "On Long Waves," Amer. J. Math. p. 211 (1914).

and area respectively of any transverse section of the canal, the equation of motion is

$$\frac{\partial^2 \eta}{\partial t^2} = \frac{g}{b} \frac{\partial}{\partial x} \left( S \frac{\partial \eta}{\partial x} \right); \quad \dots \dots \dots (1)$$

and if  $h$  be the average depth at any section,

$$S = bh,$$

and we have

$$\frac{\partial^2 \eta}{\partial t^2} = \frac{g}{b} \frac{\partial}{\partial x} \left( bh \frac{\partial \eta}{\partial x} \right), \quad \dots \dots \dots (2)$$

where  $b$  and  $h$  are both functions of  $x$ . Henceforth, by depth we shall always mean the average depth over a section.

(1).

Let us assume that equation (2) has a solution of the type

$$\eta = \phi(h, b) F. [\chi(x) \pm \sigma t], \quad \dots \dots \dots (3)$$

where  $F$  is an arbitrary function of its argument. We shall investigate the conditions under which this is possible. Substituting in (2), we have

$$\phi \cdot \frac{\sigma^2 b}{g} F'' = F \cdot \frac{\partial}{\partial x} (bh \phi') + F' \cdot \left[ hb \chi' \phi' + \frac{\partial}{\partial x} (hb \phi \chi') \right] + F'' \cdot bh \phi \chi'^2,$$

where the dashes in  $\phi'$  and  $\chi'$  mean differentiations with respect to  $x$ . Since  $F$  is arbitrary, we have

$$\chi'^2 = \frac{\sigma^2}{gh^2}, \quad \dots \dots \dots (4)$$

$$hb \phi' \chi' + \frac{\partial}{\partial x} (hb \phi \chi') = 0, \quad \dots \dots \dots (5)$$

and

$$\frac{\partial}{\partial x} (bh \phi') = 0. \quad \dots \dots \dots (6)$$

Hence

$$\chi^{(x)} = \frac{\sigma}{\sqrt{g}} \int \frac{dx}{\sqrt{h}} \quad \dots \dots \dots (4')$$

Dividing out (5) by  $bh \phi \chi'$  and integrating, we have

$$\phi^2 hb \chi'^{(x)} = \text{const.},$$

which, taken with (4), gives

$$\phi b^{\frac{1}{2}} h^{\frac{1}{2}} = \text{const.} \quad \dots \dots \dots (5')$$

This is Green's law. Equation (6) can now be written as

$$bh \frac{d}{dx} (b^{-\frac{1}{2}} h^{-\frac{1}{2}}) = \text{const.} = \alpha. \quad (6')$$

This admits of further integration. Let us now introduce a new variable given by

$$\begin{aligned} \frac{dx}{dz} &= \sqrt{h}, \\ \text{so that} \quad z &= \frac{\sqrt{g}}{\sigma} \chi. \end{aligned}$$

Then putting  $\mathfrak{S}$  for  $b^{\frac{1}{2}} h^{\frac{1}{2}}$ , equation (6') can be written as

$$\mathfrak{S}^2 \frac{d}{dz} \left( \frac{1}{\mathfrak{S}} \right) = \alpha,$$

whence by integration

$$\mathfrak{S} = \text{const.} - \alpha z.$$

We have then the following relation between  $b$ ,  $a$ , and  $\chi$ :

$$bh^{\frac{1}{2}} = \frac{\sqrt{g}}{\sigma} (\beta - \alpha \chi), \quad (6'')$$

where  $\alpha$  and  $\beta$  are any two arbitrary constants. Hence  $\phi$  varies inversely as a linear function of  $\chi$ . We have now expressed all the functions  $b$ ,  $h$ , and  $\phi$  in terms of  $\chi$ . When any one of these four functions is given as a function of  $x$ , equations (4'), (5'), and (6'') determine immediately the remaining three.

From (5') it follows that  $\phi$  is proportional to  $b^{-\frac{1}{2}} h^{-\frac{1}{2}}$ , so that Green's law of amplitude holds good in this case. But this also requires the simultaneous fulfilment of equation (6') or (6'') as an additional condition under which the law remains true. Green's restriction is that the section should vary slowly, so that the variations of  $h$  and  $b$  within the limits of a wave-length may be neglected when compared with  $h$  and  $b$  themselves. But it is evident that equation (6') or (6'') can be satisfied (at least theoretically) under more general conditions, and Green's law of amplitude will continue to hold good. It should, of course, be admitted that for rapid variations the question of reflexion would arise, but such cases we shall exclude here.

There are two arbitrary constants  $\alpha$  and  $\beta$  in (6'').  $\alpha=0$  corresponds to the case in which at every section of the

canal  $hb^2 = \text{const.}$  and the function  $\phi$  in the solution is a constant. If, now, either one of  $b$  and  $h$  is known as a function of  $x$ , the other one is given immediately by (6'') and (4'). A similar consideration also holds good for  $\beta=0$ . Hence, corresponding to any given law of breadth, there are, in general, two different laws of depth for which a motion of the type (3) can exist, and conversely, when the depth is known, there are two laws of breadth answering to it. It should also be noticed that in the wave (3) any particular phase moves with velocity  $(gh)^{\frac{1}{2}}$ ; hence when the law of variation of *breadth* is given, there are two motions possible with two different velocities of propagation. We add here certain examples.

If we take

$$hb^2 = (cx + d)^{-\frac{1}{\kappa}},$$

then we have

$$\chi = \gamma - \frac{\sigma}{\sqrt{g\alpha}} \cdot (cx + d)^{-\frac{1}{4\kappa}},$$

$$h = \alpha^2 \frac{16\kappa^2}{c^2} (cx + d)^{2 + \frac{1}{2\kappa}},$$

$$b = \frac{c}{4\kappa\alpha} (cx + d)^{-\frac{3}{4\kappa} - 1},$$

$\alpha$  and  $\gamma$  being constants.

In particular, putting  $\kappa = -\frac{3}{4}$ , we have

$$b = \text{const.}, \quad h = \frac{1}{b^2} (cx + d)^{4.3}, \quad \text{and} \quad \chi(x) = \gamma + \frac{3\sigma b}{\sqrt{gc}} (cx + d)^{1.3};$$

and putting  $\kappa = -\frac{1}{4}$ , we have

$$h = \text{const.}, \quad b = \frac{1}{\sqrt{h}} (cx + d)^2, \quad \text{and} \quad \chi(x) = \gamma + \frac{\sigma}{c\sqrt{gh}} (cx + d).$$

Again, we can easily show from (6'') that

$$\text{if } h \text{ varies as } e^{\kappa x}, \text{ then } b \propto e^{-\frac{3}{2}\kappa x} \text{ or } e^{-\frac{1}{2}\kappa x} \text{ and } \chi \propto e^{-\frac{1}{2}\kappa x},$$

$$\text{and if } h \text{ varies as } x^m, \text{ then } b \propto x^{2 - \frac{3m}{2}} \text{ or } x^{-\frac{m}{2}} \text{ and } \chi \propto x^{1 - \frac{m}{2}},$$

the second set of values of  $b$  corresponding to the case  $\alpha=0$ , or  $hb^2 = \text{const.}$  Similarly, for a definite value of  $b$  there will be two different values of  $h$  suitable for the propagation of the motion given by (3). The second sets of solutions (viz.  $h = \text{const.}, b = \text{const.}$ ) in the first two cases considered above correspond to canals with uniform sections.

If there be a definite functional relation between  $h$  and  $b$

at every section, we can proceed directly from (6'). Taking, for instance,

$$b = f(h),$$

and substituting in (6') we have on integration

$$(\beta - 4ax) = \int \left[ \frac{\sqrt{f'(h)}}{h^{\frac{1}{2}}} + 2h^{\frac{1}{2}} \frac{f''(h)}{\sqrt{f'(h)}} \right] dh, \quad \dots \quad (7)$$

which gives the necessary relation between  $a$  and  $x$ . In particular, if  $b$  varies as  $h^n$ , then the law of depth favourable for the propagation of the waves of the present type is given by

$$h \propto (\beta - 4ax)^{\frac{4}{2n+3}}.$$

The function  $bh^{\frac{1}{2}}$  plays an important part in the whole theory. The value of this function can be easily calculated from the differential equation in terms of the function  $\eta$ . For instance, if we put

$$dz_1 = \frac{dx}{\sqrt{gh}} \quad \text{and} \quad \psi = bh^{\frac{1}{2}},$$

we can write the differential equation as

$$\frac{\partial^2 \eta}{\partial t^2} = \frac{1}{\psi} \frac{\partial}{\partial z_1} \left( \psi \frac{\partial \eta}{\partial z_1} \right).$$

In this new form the two arbitrary functions in the original equation have been replaced by one. Introducing  $\frac{\partial \eta}{\partial z_1}$  both up and down on the right-hand side, we can write the equation in the form

$$\frac{\partial^2 \eta}{\partial t^2} = \frac{\partial \eta}{\partial z_1} \cdot \frac{\partial}{\partial z_1} \left\{ \log \left( \psi \frac{\partial \eta}{\partial z_1} \right) \right\},$$

from which we have on integration :

$$\psi = \frac{c}{\frac{\partial \eta}{\partial z_1}} \cdot e^{\int \frac{\partial^2 \eta}{\partial t^2} \frac{\partial \eta}{\partial z_1} dz_1 + f(t)}$$

For any given type of solution this form determines immediately the requisite value of  $\psi$ , i.e. of  $bh^{\frac{1}{2}}$ . In the present problem only those values of  $\eta$  can be of any interest to us which make  $\psi$  ultimately independent of  $t$ . It can be easily verified that this condition will be satisfied for a



solution of the form (3) if  $\phi$  be so chosen that  $\frac{1}{\phi}$  is a linear function of  $z_1$ , i.e. of  $\chi$  (cf. equation 6''). It is to be noticed that there is only one arbitrary quantity in  $\psi$ ; the constant  $c$  can be absorbed in the function of time  $f$ .

(2).

It is well known that if the width of a canal be constant at all sections while the depth varies as  $x$ , a solution of the differential equation can be obtained in the form

$$\begin{aligned}\eta &= \text{const. } J_0(\kappa x^{1/2}) \cos \kappa \sigma t \\ &= 2c \int_0^{\pi/2} \cos(\kappa x^{1/2} \sin \theta) \cos \kappa \sigma t \, d\theta \\ &= c \int_0^{\pi/2} [\cos \kappa(x^{1/2} \sin \theta + \sigma t) + \cos \kappa(x^{1/2} \sin \theta - \sigma t)] \, d\theta.\end{aligned}$$

This suggests generalization by Fourier's theorem and a solution of the form

$$\eta = \int_0^{\pi/2} [F(x^{1/2} \sin \theta + \sigma t) + F(x^{1/2} \sin \theta - \sigma t)] \, d\theta,$$

where  $F$  is an even function of its argument. This leads us to try the following integral:

$$\eta = \phi(b, h) \int_0^{\pi/2} [F\{\chi(x) \sin \theta + \sigma t\} + F\{\chi(x) \sin \theta - \sigma t\}] \, d\theta \quad \dots \dots (8)$$

as a solution of equation (2), where  $F$  is an arbitrary even function. Substituting in the differential equation, and after a single integration by parts, we have

$$\chi'^2 = \frac{\sigma^2}{gh}, \quad \dots \dots (9)$$

$$\frac{d}{dx} \left( bh \frac{d\phi}{dx} \right) = 0, \quad \dots \dots (10)$$

$$\frac{d}{dx} (hb \phi \chi') + hb \chi' \frac{d\phi}{dx} - hb \phi \chi'^2 = 0. \quad \dots \dots (11)$$

From (10) we have

$$bh \frac{d\phi}{dx} = \text{const.}, \quad \dots \quad (10')$$

and the equation (11) immediately admits of the integral

$$hb \phi^2 \frac{\chi'(x)}{\chi(x)} = \text{const.};$$

whence we have

$$\phi = \frac{c}{\sqrt{hb}} \sqrt{\frac{\chi(x)}{\chi'(x)}}, \quad \dots \quad (11')$$

$c$  being a constant. Equation (10') can now be written as

$$\left[ \frac{1}{\sqrt{\frac{1}{hb} \frac{\chi(x)}{\chi'(x)}}} \right]^2 \frac{d}{dx} \left[ \sqrt{\frac{1}{hb} \frac{\chi(x)}{\chi'(x)}} \right] = -\kappa \frac{\chi'(x)}{\chi(x)},$$

where  $\kappa$  is a constant; from this we have on integration

$$bh = [\alpha + \kappa \log \chi(x)]^2 \frac{\chi(x)}{\chi'(x)}, \quad \dots \quad (12)$$

and consequently

$$\phi = c[\alpha + \kappa \log \chi(x)]^{-1}. \quad \dots \quad (13)$$

In this case also  $\phi$  is expressed explicitly as a function of  $\chi$ , though its dependence on  $h$  and  $b$  is not so simple as in (5''). When any one of the functions  $b$ ,  $h$ ,  $\chi$ , and  $\phi$  is known as a function of  $x$ , equations (9), (12), and (13) determine the values of the other three in such a way that equation (2) has the integral (8) for a solution. One of these four functions we can choose always arbitrarily. The appearance of two arbitrary constants  $\alpha$  and  $\kappa$  in (12) indicates that here also, as in the previous case, corresponding to any value of either one of  $h$  and  $b$  there exist two different values of the other function such that a motion of the present type may become possible. For the particular value

$$\chi(x) = \sqrt{x}$$

we have

$$h = \frac{4\sigma^2}{g}x, \quad bh = 2x[\alpha + \frac{1}{2}\kappa \log x]^2$$

and

$$\eta = c(\alpha + \frac{1}{2}\kappa \log x)^{-1} \int_0^{\pi/2} [F(x^{1/2} \sin \theta + \sigma t) + F(x^{1/2} \sin \theta - \sigma t)] d\theta.$$

If in these results we put  $\kappa=0$ , we pass on to the case of constant breadth and of the depth varying as  $x$ . Secondly, if we put

$$h = \text{const.} \quad \text{and} \quad \chi'(x) = \frac{\sigma}{\sqrt{gh}} = \alpha,$$

then

$$\chi(x) = \alpha x + \beta \quad \text{and} \quad b = \left(\frac{x}{h} + \frac{\beta}{\alpha h}\right) \{c + \kappa \log(\alpha x + \beta)\}^2$$

and

$$\eta = c' \{c + \kappa \log(\alpha x + \beta)\}^{-1} \int_0^{\pi/2} [F(\alpha x + \beta \sin \theta + \sigma t) + F(\alpha x + \beta \sin \theta - \sigma t)] d\theta.$$

In this result, if we put  $\kappa=0$ , then we have

$$b \propto (\alpha x + \beta).$$

Again, putting  $\chi(x) = e^{mx}$ , we have

$$h = \frac{\sigma^2}{gm^2} e^{-2mx}, \quad b = \frac{gm}{\sigma^2} e^{2mx} (\alpha + \kappa mx)^2$$

and

$$\eta = c(\alpha + \kappa mx)^{-1} \int_0^{\pi/2} [F(e^{mx} \sin \theta + \sigma t) + F(e^{mx} \sin \theta - \sigma t)] d\theta.$$

(3).

The solution found in § 1 can be generalized by assuming that  $\eta$  depends not only on  $F$ , but also on the differential coefficients of this function. Following the suggestion of Wedderburn \*, let us put

$$\begin{aligned} \eta = & \phi_0(h, b) F[\chi(x) + \sigma t] + \phi_1(h, b) F'[\chi(x) + \sigma t] \\ & + \phi_2(h, b) F''[\chi(x) + \sigma t] + \dots + \phi_n(h, b) F^n[\chi(x) + \sigma t]. \end{aligned} \quad (14)$$

\* *Loc. cit*

Substituting in equation (2) and equating coefficients of  $F, F', \dots$ , we have

$$\left. \begin{aligned} \frac{\partial}{\partial x} (bh\phi_0') &= 0, \\ bh\chi'\phi_0' + \frac{\partial}{\partial x} (bh\chi'\phi_0 + bh\phi_1') &= 0, \\ bh\chi'\phi_1' + \frac{\partial}{\partial x} (bh\phi_1\chi_1' + bh\phi_2') &= \left(\frac{\sigma^2}{g} - h\chi'^2\right) b\phi_0, \\ bh\chi'\phi_2' + \frac{\partial}{\partial x} (bh\phi_2\chi' + bh\phi_3') &= \left(\frac{\sigma^2}{g} - h\chi'^2\right) b\phi_1, \\ &\dots \dots \dots \\ bh\chi'\phi_n' + \frac{\partial}{\partial x} (bh\phi_n\chi') &= \left(\frac{\sigma^2}{g} - h\chi'^2\right) b\phi_{n-1}, \\ 0 &= \left(\frac{\sigma^2}{g} - h\chi'^2\right) b\phi_n. \end{aligned} \right\} \quad (15)$$

The first and the last two equations give immediately on integration

$$bh\phi_0' = \text{const.}, \quad \phi_n = c_n b^{-\frac{1}{2}} h^{-\frac{1}{2}}, \quad \text{and} \quad \chi' = \frac{\sigma}{\sqrt{gh}},$$

whereas the relation between any two consecutive  $\phi$ 's is given by the remaining equations of (15). Writing the general equation in the form

$$2bh\chi'\phi'_{r-1} + \phi_{r-1} \frac{\partial}{\partial x} (bh\chi') + \frac{\partial}{\partial x} (bh\phi'_r) = 0,$$

and expressing  $\chi'$  in terms of  $h$  and making the following substitutions :

$$bh^{1/2} = \mathfrak{s}, \quad dz = \frac{dx}{\sqrt{h}},$$

we can also write it as follows:

$$2\mathfrak{s} \frac{\partial \phi_{r-1}}{\partial z} + \phi_{r-1} \frac{\partial \mathfrak{s}}{\partial z} + \frac{\sqrt{g}}{\sigma} \frac{\partial}{\partial z} \left( \mathfrak{s} \frac{\partial \phi_r}{\partial z} \right) = 0. \quad (15')$$

This is the general equation to determine  $\phi_r$ , the two extreme equations having the integrals

$$\phi_n = c_n \mathfrak{s}^{-\frac{1}{2}} \quad \text{and} \quad \mathfrak{s} \frac{\partial \phi_0}{\partial z} = \text{const.}$$

In its general form this equation is difficult to handle, but particular solutions may sometimes be obtained easily. For instance, if we assume  $\mathfrak{S} = z^m$  and consequently

$\phi_n = c_n z^{-\frac{m}{2}}$ , we can easily show that  $\phi_{n-r}$  is of the form

$$\phi_{n-r} = c_{n-r} z^{-\frac{m}{2}-r},$$

where the constant  $c_{n-r}$  is given by the recurrence formula

$$2rc_{n-r} + \frac{\eta}{\sqrt{\sigma}} \left( \frac{m}{2} - r \right) \left( \frac{m}{2} + r - 1 \right) c_{n-r+1} = 0.$$

Now we have to choose  $m$  in such a way that the equation

$$\mathfrak{S} \frac{\partial \phi_0}{\partial z} = \text{const.}$$

is automatically satisfied. Here we distinguish between two cases. If we take  $\phi_0 (\neq 0)$  itself to be constant, then we must also take

$$\frac{m}{2} + n = 0, \text{ i. e. } m = -2n,$$

and

$$\mathfrak{S} = z^{-2n}, \quad \phi_{n-r} = c_{n-r} z^{n-r};$$

or if we take  $\phi_0 (\neq 0)$  to be different from constant, we have to put

$$\frac{m}{2} - n - 1 = 0, \text{ i. e. } m = 2(n+1),$$

and

$$\mathfrak{S} = z^{2(n+1)}, \quad \phi_{n-r} = c_{n-r} z^{-(n+r+1)}.$$

The corresponding values of  $b$  and  $h$  can be easily found.

We can get a completely soluble case if we take  $\eta$  to consist of two terms only, *e. g.*

$$\eta = \phi_0 F + \phi_1 F'.$$

We have, as before,

$$\chi'^2 = \frac{\sigma^2}{gh}, \quad \phi_1 = c_1 b^{-\frac{1}{2}} h^{-\frac{1}{2}}, \quad bh\phi_0' = \text{const.} = \alpha,$$

and

$$\frac{\partial}{\partial x} (bh\phi_0\chi') + \alpha\chi' + \frac{\partial}{\partial x} (bh\phi_1') = 0;$$

integrating, we have

$$bh\phi_0\chi' + \alpha\chi + bh\phi_1' = \beta \text{ (const.)}.$$

Substituting the value of  $\phi_0$  obtained from this equation

in the third of the above equations and introducing a slightly different notation,

$$\Theta = b^{-\frac{1}{2}} h^{-\frac{1}{2}},$$

we have ultimately

$$\frac{d}{dz} \left[ -\frac{c_1 \sqrt{g}}{\sigma} \frac{d\Theta}{dz} + \left( \beta \frac{\sqrt{g}}{\sigma} - \alpha z \right) \Theta^2 \right] = \alpha \Theta^2.$$

This is a non-linear equation and has no simple general solution. A particular solution is, however, given by

$$\Theta = -\frac{c_1}{\beta} \cdot \frac{1}{z}.$$

But we get a completely soluble case if we put  $\alpha=0$ , which corresponds to  $\phi_0 = \text{const.} = c_0$  and to the solution

$$\eta = c_0 F \left( \frac{\sigma}{\sqrt{g}} z + \sigma t \right) + c_1 b^{-\frac{1}{2}} h^{-\frac{1}{2}} F' \left( \frac{\sigma}{\sqrt{g}} z + \sigma t \right).$$

It can be shown that in this case the above equation has solutions of the form

$$\Theta = \kappa_1 \sigma' \frac{e^{-\sigma' \kappa_1 \kappa_2 (z + \kappa_3)} + e^{\sigma' \kappa_1 \kappa_2 (z + \kappa_3)}}{e^{-\sigma' \kappa_1 \kappa_2 (z + \kappa_3)} - e^{\sigma' \kappa_1 \kappa_2 (z + \kappa_3)}},$$

where  $\sigma' = \frac{\sigma^{1/2}}{g^{1/4}}$  and  $\kappa_1, \kappa_2, \kappa_3$  are three constants of which  $\kappa_1$  and  $\kappa_2$  are connected by the relation  $\frac{c_0}{c_1} = \kappa_1^2 \kappa_2$ ; or

$$\Theta = \kappa_1 \sigma' \tan \sigma' \kappa_1 (\kappa_3 - \kappa_2 z),$$

depending on the signs of the constants in the above differential equation (when  $\beta \neq 0$ ). The simplest case, however, arises when we put  $\beta$  also  $= 0$ . The following illustrations are then perhaps interesting:—

$$h = \text{const.},$$

$$b = \frac{1}{\sqrt{h} x^2} \quad \text{and} \quad \eta = c_0 F \left( \frac{x}{\sqrt{gh}} + t \right) + c_1 x F' \left( \frac{x}{\sqrt{gh}} + t \right);$$

$$b = \text{const.},$$

$$h = \frac{x^4}{b^2} \quad \text{and} \quad \eta = c_0 F \left( -\frac{b}{\sqrt{g} x} + t \right) + \frac{c_1}{x} F' \left( -\frac{b}{\sqrt{g} x} + t \right).$$

In such cases we can, of course, make use of the solution

of the general equation (15') given above. In the above examples the solutions correspond to  $\beta=0$ ; other solutions corresponding to the constant values of  $h$  and  $b$  can be easily found from the general solutions given above.

(4).

In the manner of the preceding section we can find solutions of equation (2) in terms of the integral of § 2 and its differential coefficients. We discuss here a case which is simple and completely integrable. We suggest the following solution :

$$\eta = \phi(h, b) \frac{\partial}{\partial x} \int_0^{\pi/2} [F\{\chi(x) \sin \theta + \sigma t\} + F\{\chi(x) \sin \theta - \sigma t\}] d\theta, \quad \dots (16)$$

where  $F$  is an even function of its argument. Substituting in the differential equation and proceeding in the usual way, we get the following conditions:

$$\left. \begin{aligned} \chi'^2 &= \frac{\sigma^2}{gh}, \\ \phi^2 h b \frac{\chi'^3(x)}{\chi(x)} &= \text{const.}, \\ \frac{d}{dx} \left[ b h \frac{d}{dx} (\phi \chi') \right] + b h \phi \frac{\chi'^3}{\chi^2} &= 0. \end{aligned} \right\} \quad \dots (17)$$

Eliminating  $\phi$  and  $h$  from the third equation with the help of the two preceding ones, we have

$$\frac{d}{dx} \left[ \frac{b}{\chi'^2} \cdot \frac{d}{dx} \left( \sqrt{\frac{\chi \chi'}{b}} \right) \right] + \frac{b}{\chi^2} \sqrt{\frac{\chi \chi'}{b}} = 0.$$

Writing this equation in the form

$$\chi \frac{d}{dx} \left[ \frac{b}{\chi \chi'} \cdot \frac{\chi}{\chi'} \frac{d}{dx} \left( \sqrt{\frac{\chi \chi'}{b}} \right) \right] + \sqrt{\frac{b}{\chi \chi'}} = 0,$$

and making the following substitutions:

$$\sqrt{\frac{\chi \chi'}{b}} = \xi \quad \text{and} \quad \frac{\chi}{\chi' dx} = \frac{\chi}{dx} = \frac{1}{dy}, \quad \text{i.e.} \quad y = \log \chi,$$

we have after simplification

$$\frac{d^2}{dy^2} \left( \frac{1}{\xi} \right) - \frac{1}{\xi} = 0.$$

This has the solutions

$$\frac{1}{\xi} = e^y \text{ and } e^{-y};$$

whence we have

$$\sqrt{\frac{\chi\chi'}{b}} = \chi \text{ and } \frac{1}{\chi}.$$

In the first case we have

$$\left. \begin{aligned} b = \frac{\chi'}{\chi} \quad \text{and} \quad h = \frac{\sigma^2}{g} \cdot \frac{1}{\chi'^2}, \\ \text{and in the second} \\ b = \chi^3 \chi' \end{aligned} \right\} \dots (18)$$

with the same value for  $h$ . We can now easily find

$$\phi = \frac{c\sqrt{g}}{\sigma} \sqrt{\frac{\chi}{b\chi'}} \dots (19)$$

If we choose  $\chi$  arbitrarily we shall have two corresponding values for  $b$ , and if we choose  $b$  arbitrarily we shall have two corresponding values for  $\chi$  and consequently two values for  $h$  also.

The following cases are perhaps interesting:—

$$\chi(x) = x^n, \quad h = \frac{\sigma^2}{gn^2} x^{2(1-n)}, \quad b = nx^{4n-1} \text{ or } \frac{n}{x},$$

and

$$\eta = \kappa x^{1-2n} \frac{\partial}{\partial x} \int_0^{\pi/2} [F\{x^n \sin \theta + \sigma t\} + F\{x^n \sin \theta - \sigma t\}] d\theta$$

$$\text{or} \quad \kappa x \frac{\partial}{\partial x} \int_0^{\pi/2} [F\{x^n \sin \theta + \sigma t\} + \dots] d\theta$$

according as  $b$  is equal to  $nx^{4n-1}$  or  $nx^{-1}$  respectively ( $\kappa$  being a constant).

Putting  $n=1$ , we have the case of constant depth, and

$$h = \frac{\sigma^2}{g}, \quad b = x^3 \text{ or } \frac{1}{x},$$

and

$$\eta = \frac{\kappa}{x} \frac{\partial}{\partial x} \int_0^{\pi/2} [F(x \sin \theta + \sigma t) + \dots] d\theta$$

$$\text{or} \quad \kappa x \frac{\partial}{\partial x} \int_0^{\pi/2} [F(x \sin \theta + \sigma t) + \dots] d\theta$$

respectively.

Again, for constant values of  $b$  we have the solutions:

$$b = \text{const.}, \quad h = \frac{8\sigma^2}{g\sqrt{b}} x^{3/2} \text{ or } \frac{\sigma^2}{gb^2} e^{-2bx},$$



and

$$\eta = \kappa x^{\frac{1}{2}} \frac{\partial}{\partial x} \int_0^{\pi/2} [F(\sqrt{4bx^{\frac{1}{2}}} \sin \theta + \sigma t) + \dots] d\theta$$

or

$$\kappa \frac{\partial}{\partial x} \int_0^{\pi/2} [F(e^{bx} \sin \theta + \sigma t) + \dots] d\theta,$$

corresponding to the first or second value of  $h$ . The last solution has been given by Wedderburn.

Again, putting

$$\chi(x) = e^{\lambda x},$$

we have

$$h = \frac{\sigma^2}{g\lambda^2} e^{-2\lambda x}, \quad b = \lambda \text{ or } \lambda e^{4\lambda x}.$$

The solution corresponding to the constant value of  $b$  is the one already given above; that corresponding to the second value of  $b$  is

$$\eta = \kappa e^{-2\lambda x} \frac{\partial}{\partial x} \int_0^{\pi/2} [F(e^{\lambda x} \sin \theta + \sigma t) + F(e^{\lambda x} \sin \theta - \sigma t)] d\theta.$$

*Note.*—The results of § 1 can be deduced more simply if the equation of motion (2) be slightly transformed as follows. Using the same notation as in § 1, we can write (2) as

$$\frac{\partial^2(\eta\mathfrak{S})}{\partial t^2} = g \frac{\partial}{\partial z} \left( \mathfrak{S}^2 \frac{\partial \eta}{\partial z} \right),$$

which is the same as

$$\frac{\partial^2(\eta\mathfrak{S})}{\partial t^2} = g \left( \frac{\partial^2(\eta\mathfrak{S})}{\partial z^2} - \eta \frac{\partial^2 \mathfrak{S}}{\partial z^2} \right).$$

From this it at once follows that  $\eta\mathfrak{S}$  satisfies the usual wave equation, and is equivalent to an arbitrary function of the form  $F(z \pm \sqrt{g}t)$  if  $\mathfrak{S}$  satisfies the equation

$$\frac{\partial^2 \mathfrak{S}}{\partial z^2} = 0,$$

or  $\mathfrak{S}$  is a linear function of  $z$ , which is the same result as equation (6). A clue to the other types of solutions of equation (2) can be obtained if we take the relation between  $\mathfrak{S}$  and  $z$  to be given by

$$\frac{1}{\mathfrak{S}} \frac{\partial^2 \mathfrak{S}}{\partial z^2} = \phi(z),$$

$\phi(z)$  being a given function of  $z$ . Then the whole problem of wave motion in canals reduces to the solution of an equation of the form

$$\frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 u}{\partial z^2} - \phi(z)u.$$

VII. *The Diameters of the Atoms of the Inert Gases.*By J. E. CALTHROP, *B.A.(Cantab.), B.Sc.(Lond.)*.\*

VALUES for the radii of the atoms of the inert gases have been given by Davey † from a consideration of the packing radii of alkali and halogen ions in crystal lattices. These are much greater than those given by Prof. W. L. Bragg, and in most cases even greater than the estimates of Prof. Rankine from viscosity data and from Chapman's formula:—

$$\sigma^2 = \frac{0.4915\bar{V}}{\sqrt{2}n\pi\eta\left(1 + \frac{c}{T}\right)},$$

in which

 $\sigma$  = molecular diameter, $\rho$  = density, $\bar{V}$  = mean molecular velocity, $n$  = number of molecules per c.c., $\eta$  = viscosity, $T$  = absolute temperature, $c$  = Sutherland's constant.

Davey finds that Rankine's results are related to his by the formula  $(R - 0.35)\sqrt{2} = D$ , where  $R$  is the Rankine radius and  $D$  his own. Further, he suggests that Chapman's formula could be modified empirically to give results which agree with his crystal method, though he can find no theoretical basis for such a modification.

In a recent paper ‡ he states a new law: "The ratio of the radii of any two simple atoms belonging to the same vertical column in the periodic table is the same as the ratio of the radii of any other two simple atoms in the same rows of the table, and in a common vertical column." This enables him to predict the diameters of the atoms of certain elements, including helium, which had not been deduced previously from crystal data.

His value for the diameter of the Helium atom is  $2.06 \text{ \AA}$ , which is near Rankine's value of  $2.16 \text{ \AA}$ .

It is of interest to find what value is obtained from the refractivity, for we have recently § pointed out that the refractivities and the Bragg values of the atomic diameters of the inert gases are related by the equation  $(\mu - 1) = 1.23N\sigma^3$ ,

\* Communicated by the Author.

† Physical Review, xxii. p. 211 (1923).

‡ Physical Review, xxiii. p. 318 (1924).

§ Phil. Mag. xlvii. p. 772 (1924).

where  $(\mu-1)$  is the refractivity of the gas,  $N$  is the number of atoms per c.c. and is taken as  $2.705 \times 10^{19}$ , and  $\sigma$  is the atomic diameter.

If we may include helium in the same group, and use the refractivity  $34.9 \times 10^{-6}$  given by Cuthbertson, we obtain a diameter of  $1.02 \text{ \AA}$ . This is in good agreement with the earlier estimate of M. Zierucci\* from the temperature of fusion. He gave the equation

$$T_f = 79D_A - 81,$$

where  $T_f$  is the absolute temperature of fusion, and  $D_A$  is the atomic diameter in Ångström units.  $T_f$  is near  $1^\circ$  for helium, and the diameter obtained is  $1.04 \text{ \AA}$ .

We may find how far the Davey values obey an equation of the type  $(\mu-1) = KN\sigma^3$ , in which  $K$  is a constant which holds for the Bragg values. In the following table  $K$  is calculated both from the data of Davey and Bragg, except that we consider  $1.02 \text{ \AA}$  to be the "Bragg" value for helium.

Element.	Refractivity $\times 10^6$ .	DAVEY.		BRAGG.	
		$\sigma$ .	K.	$\sigma$ .	K.
He .....	34.9	$2.06 \text{ \AA}$	0.15	$1.02 \text{ \AA}$	1.23
Ne .....	68.7	2.52	0.16	1.30	1.16
Ar .....	283.7	3.14	0.34	2.05	1.24
Kr .....	427.3	3.42	0.39	2.35	1.24
Xe .....	702.0	3.94	0.42	2.70	1.35

Thus the Davey estimates do not appear to give so simple a relation between the refractivities and diameters as do those of Bragg.

It is noticeable, however, that the differences between the two sets of diameters are fairly constant. Consequently, if we take the mean of these differences,  $1.13 \text{ \AA}$ , and employ a formula

$$(\mu-1) = KN(\sigma - 1.13)^3$$

where  $K$  is now the Davey diameter, we get the following values of  $K$  :—

Element.	$K = \frac{(\mu-1)}{N(\sigma-1.13)^3}$ .
He .....	1.60
Ne .....	0.95
Ar .....	1.29
Kr .....	1.32
Xe .....	1.17

\* *Nuovo Cimento*, xxii. p. 189 (1921).

The mean value of  $K$  is 1.27, and thus we might suggest  $(\mu-1)=1.27N(\sigma-1.13)^3$  as the equation of the Davey values. On the whole, the evidence of refractivity appears to be in favour of the Bragg diameters, as there seems no reason why the refractivity should be uninfluenced by diameters less than 1.13 Å.

East London College,  
May 6th, 1924.

VIII. *On the Chance of an Electron being Ejected Photoelectrically from an Atom by X-rays.* By G. E. M. JAUNCEY, D.Sc., Assistant Professor of Physics, Washington University, U.S.A.\*

### 1. Introduction.

**T**HE total mass absorption coefficient of X-rays in matter is made up of two parts thus:

$$\mu/\rho = \tau/\rho + \sigma/\rho, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $\tau/\rho$  is the true mass absorption coefficient and  $\sigma/\rho$  is the mass scattering coefficient, which for light elements and soft X-rays is of the order 0.2 gram<sup>-1</sup>. From the true absorption coefficient, the true absorption coefficient per atom, or the true atomic absorption coefficient, may be found by multiplying  $\tau/\rho$  by the atomic weight and dividing by Avogadro's number. Owen† and others have found the empirical relation that the true atomic absorption coefficient, which we shall represent by  $\tau/\nu$ , is equal to  $kN^4\lambda^3$ , where  $N$  is the atomic number of the absorbing substance,  $\lambda$  is the wave-length of the X-rays, and  $k$  is a constant. The quantity  $k$ , however, is only constant within certain limits. When a K, L, or M etc. absorption limit is passed the value of  $k$  changes abruptly.

The energy which is lost from the primary beam due to true absorption goes into the production of photoelectrons and K, L, M etc. characteristic radiations. However, it will be assumed that the production of characteristic radiations is a secondary process, and that the primary effect of the X-rays is to produce photoelectrons. A photoelectron cannot be ejected from an atom unless the energy of the

\* Communicated by the Author.

† E. A. Owen, Proc. Roy. Soc., A. xciv. p. 522 (1918).

X-ray quantum is greater than the binding energy of the electron. This binding energy is determined by the K, L, M etc. absorption limits. It so happens that according to Moseley's law the K absorption limit wave-length is very nearly inversely proportional to the square of the atomic number. Now M. de Broglie \* has shown that, when the wave-length of the X-rays is short enough to excite the K radiations of a substance, the number of photoelectrons ejected from the K energy level is greatly in excess of the number ejected from the L and M energy levels. It seems, then, that so long as the K radiations are excited the greater part of the energy lost from the primary beam goes into the production of photoelectrons ejected from the K level. Since the binding energy of the electrons in the K level is proportional to  $N^2$  approximately, it seems that the true atomic absorption coefficient varies as the square of the binding energy of the electrons in the K level, provided that the K radiations are excited.

## 2. *Probability of Photoelectric Emission.*

The above considerations led the writer to make the hypothesis that the chance of an electron being ejected photoelectrically from one of the K, L, or M etc. levels is proportional to the square of the binding energy of the electron in the level from which it is ejected, provided that the wave-length is short enough to eject the electron from the level and provided that the wave-length of the X-rays is kept constant. Let  $\lambda_K$ ,  $\lambda_L$ , and  $\lambda_M$  be the absorption limit wave-lengths for the K, L, and M radiations respectively from a given absorbing material. The binding energies of the electrons in the levels are then inversely proportional to these quantities respectively. Each atom has  $n_K$ ,  $n_L$ , etc. electrons in the K, L, etc. levels respectively. On the writer's hypothesis the chance of a K electron being ejected from an atom is proportional to  $n_K/\lambda_K^2$ , the chance of an L electron being ejected is proportional to  $n_L/\lambda_L^2$ , and so on for the electrons in the other levels. Assuming that the chance of an atom being doubly ionized is negligible, we then have that the chance of any one of the K, L, or M etc. electrons being ejected from an atom is proportional to

$$P = n_K/\lambda_K^2 + n_L/\lambda_L^2 + n_M/\lambda_M^2 + \dots \dots \dots (2)$$

Keeping the wave-length constant and varying the absorber,

\* M. de Broglie, *Jour. d. Phys. et Rad.* ii. p. 265 (1921).

the atomic absorption coefficient should be proportional to  $P$ . If the wave-length  $\lambda$  of the primary X-rays is longer than  $\lambda_K$ , the  $K$  term drops out and so on. Since the true absorption coefficient also varies as  $\lambda^3$ , we may say that the chance of an electron being ejected from an atom is proportional to  $\lambda^3 P$ . The true atomic absorption coefficient being supposed to be due to the ejection of photoelectrons, this quantity should be given by

$$\tau/\nu = G\lambda^3(n_K/\lambda_K^2 + n_L/\lambda_L^2 + \dots), \quad (3)$$

where  $G$  is a constant. The relation (3) has been obtained theoretically by A. H. Compton\* on the classical theory and by L. de Broglie† on the quantum theory. However, in both cases the theoretical approach involves so many other factors that it is difficult to see what assumption it is that results in the  $n_K/\lambda_K^2 + \text{etc.}$  term in the absorption equation (3). On the writer's view this term merely means that the probability of photoelectric emission is proportional to the square of the binding energy. The writer therefore suggests that Owen's law be replaced by the following empirical law :

“The chance of an electron being ejected photoelectrically from an atom by X-rays is proportional to the cube of the wave-length of the X-rays and to the square of the binding energy of the electron to the atom, provided that the wave-length is short enough to eject the electron.”

This law will now be supported by showing from experimental evidence that the true atomic absorption coefficient is proportional to  $\lambda^3 P$ . The values of  $\lambda_K$ ,  $\lambda_L$ ,  $\lambda_M$  for various elements are given in Table I. These are averages of values given by Foote and Mohler‡, Hughes§, Kurth||, and Sommerfeld¶. The L and M absorption limits have a fine structure, but in the table only the average wave-lengths are given. Some of the values have been obtained by interpolation.

\* A. H. Compton, Bull. Nat. Res. Council, xx. p. 39.

† L. de Broglie, *Jour. de Phys. et Rad.* iii. p. 33 (1922).

‡ Foote and Mohler, Phys. Rev. xix. p. 434 (1922).

§ A. L. Hughes, Phil. Mag. xliii. p. 145 (1922).

|| E. H. Kurth, Phys. Rev. xviii. p. 461 (1921).

¶ A. Sommerfeld, *Atombau und Spektrallinien*, pp. 227-229

TABLE I.  
Absorption Limits in Ångström Units.

Element.	Atomic Number.	$\lambda_K$ .	$\lambda_L$ .	$\lambda_M$ .
C .....	6	46.2	368	—
Al .....	13	7.95	150	326
Fe .....	26	1.74	16.3	54.3
Cu .....	29	1.38	12.3	41.6
Mo .....	42	.618	4.8	18.6
Ag .....	47	.485	3.5	15.0
Pb .....	82	.141	.85	4.5

In Table II. are shown the values of  $n_K$ ,  $n_L$ ,  $n_M$ ,  $n_K/\lambda_K^2$ ,  $n_L/\lambda_L^2$ , and  $n_M/\lambda_M^2$  for the various elements,  $\lambda_K$ ,  $\lambda_L$ , and  $\lambda_M$  being in Ångström units.

TABLE II.

Element.	$n_K$ .	$n_L$ .	$n_M$ .	$n_K/\lambda_K^2$ .	$n_L/\lambda_L^2$ .	$n_M/\lambda_M^2$ .
C .....	2	4	0	.00094	.00003	—
Al .....	2	8	3	.0316	.00036	.00003
Fe .....	2	8	16	.66	.0302	.0055
Cu .....	2	8	18	1.058	.0532	.0105
Mo .....	2	8	18	5.24	.349	.052
Ag .....	2	8	18	8.52	.65	.08
Pb .....	2	8	18	100.5	11.1	.9

The values of  $G$  obtained by dividing the experimental value of the true atomic absorption coefficient by  $\lambda^3 P$  are shown in the sixth column of Tables III., IV., and V. These values of  $G$  are for the case where  $\lambda$ ,  $\lambda_K$ ,  $\lambda_L$ , etc. are measured in Ångström units. In these tables the true mass absorption coefficients are obtained by subtracting the mass scattering coefficient from the respective values of the total absorption coefficients given by A. H. Compton in a table in the Bulletin of the National Research Council on Secondary Radiations produced by X-rays. The mass scattering coefficient used in calculating the true absorption coefficient is not that given by Thomson's theory\*, viz.,  $0.4019 \times p/w \text{ gram}^{-1}$ , where  $p$  is the number of electrons per atom and  $w$  the atomic weight. The scattering coefficient is

\* J. J. Thomson, 'Conduction of Electricity through Gases,' p. 325.

somewhat doubtful. A. H. Compton \* and the writer † have shown in their quantum theories of scattering that the scattering coefficient is  $1/(1+2a)$  times the Thomson coefficient, where  $a=h/mc\lambda$ . Thus for  $\lambda=0.35$  Å.U.,

$$a=0.24/0.35=0.69,$$

and the mass scattering coefficient for carbon is

$$0.201/1.138=0.176.$$

The total mass absorption coefficient in carbon is given in Compton's table as 0.219, leaving 0.043 as the true absorption coefficient.

TABLE III.

Wave-length . . . 0.35 Å.U.

Characteristic Radiations Excited.	Element.	$\tau/\rho$ Experimental.	$\tau/\nu \times 10^{23}$ Experimental.	P.	$\tau/\nu$ $\lambda^3 P \times 10^{20}$ .
K, L .....	C .....	0.43	0.84	0.0097	2.01
K, L, M .....	Al .....	0.56	2.49	0.032	1.80
K, L, M .....	Fe.....	4.59	42.4	0.695	1.42
K, L, M .....	Cu ...	6.77	70.6	1.122	1.46
K, L, M .....	Mo ...	18.9	299.0	5.64	1.24
K, L, M .....	Ag.....	27.0	481.0	9.25	1.21
L, M .....	Pb.....	22.4	765.0	12.0	1.48

TABLE IV.

Wave-length . . . 0.70 Å.U.

Characteristic Radiations Excited.	Element.	$\tau/\rho$ Experimental.	$\tau/\nu \times 10^{23}$ Experimental.	P.	$\tau/\nu$ $\lambda^3 P \times 10^{20}$ .
K, L .....	C .....	0.34	0.67	0.0097	2.01
K, L, M .....	Al .....	4.76	21.1	0.032	1.92
K, L, M .....	Fe... ..	37.7	349.0	0.695	1.46
K, L, M .....	Cu ...	52.5	547	1.122	1.42
L, M .....	Mo ...	18.5	298	0.401	2.16
L, M .....	Ag.....	31.5	561	0.73	2.24
L, M .....	Pb.....	163.6	5540	12.0	1.34

\* A. H. Compton, *Phys. Rev.* xxi. p. 483 (1923).

† G. E. M. Jauncey, *Phys. Rev.* xxii. p. 233 (1923), and xxiii. p. 313 (1924).



TABLE V.

Wave-length . . . 1.0 Å.U.

Characteristic Radiations (Excited.)	Element.	$\tau/\rho$ Experimental.	$\tau/\nu \times 10^{23}$ Experimental.	P.	$\frac{\tau/\nu}{\lambda^3 P} \times 10^{20}$
K, L .....	C .....	1.07	2.12	.0097	2.18
K, L, M .....	Al ... ..	13.6	60.5	.032	1.89
K, L, M .....	Fe .....	90.0	832	.695	1.20
K, L, M .....	Cu .....	146.0	1518	1.122	1.35
L, M .....	Mo ... ..	53.0	840	.401	2.10
L, M .....	Ag .....	87.0	1550	.73	2.12

Examining values of  $G$  given in the last columns of Tables III., IV., and V., we see that  $G$  is fairly constant, varying only by a factor of 1.85 from the smallest to the largest value, whereas in Table III.  $\tau/\nu$  varies by a factor of about 9000. Furthermore, it is seen that the value of  $G$  remains approximately constant when an absorption limit is passed, as, for instance, in Table III. when we pass from silver to lead. The lack in the constancy of  $G$  may possibly be due to several causes. First, the absorption wave-length limits are not known to a high degree of accuracy, especially in the case of the L and M absorption limits. Then, too, the N, O, P, etc. limits have not been considered. Second, the total absorption coefficients are somewhat uncertain, as in the case of the elements of low atomic number very great purity is necessary and in the case of the elements of high atomic number only very small thicknesses can be used. Third, each of the L, M, etc. absorption limits has a fine structure. Instead of  $n_L/\lambda_L^2$  we should write the sum of three terms, there being three L absorption limits. To make this correction it would be necessary to know the numbers of electrons per atom in the  $L_1$ ,  $L_2$ , and  $L_3$  energy levels. Fourth, there is great uncertainty in the value assigned to the scattering coefficient. A. H. Compton\* has measured the spectrum of scattered X-rays and has found that part of the scattered radiation suffers a change of wave-length while part of it does not. It seems probable that the scattering coefficient of the unmodified radiation would be given by Thomson's value. Instead, therefore, of subtracting  $0.2/(1+2a)$  from the total absorption, we should subtract some quantity between this and 0.2 in order to obtain the true absorption coefficient. It seems possible that if all

\* A. H. Compton, Phys. Rev. xxii. p. 409 (1923).

these sources of error could be eliminated  $G$  might be found to be a constant. The average of all the values of  $G$  in Tables III., IV., and V. is  $1.71 \times 10^{-20}$ .

Further, it is found experimentally that the absorption, "jump" for a given absorbing substance when the X-rays are decreased in wave-length past the K absorption limit decreases with increasing atomic number. Recently Allen \* and Warburton and Richtmeyer † have shown that the ratio of the  $K + L + M + \dots$  absorption to the  $L + M + \dots$  absorption at the K absorption limit is about 7, but decreases for high atomic numbers. On the present view this ratio should be

$$\frac{n_K/\lambda_K^2 + n_L/\lambda_L^2 + n_M/\lambda_M^2 + \dots}{n_L/\lambda_L^2 + n_M/\lambda_M^2 + \dots} \dots \dots (4)$$

Referring to Table II., it is seen that this ratio decreases from 19.5 for Fe to 9.4 for Pb, which is in the general direction of the experimental results.

### 3. Discussion.

The writer believes that considerable experimental evidence has been quoted to support the proposition that the chance of an electron being ejected photoelectrically from an atom (*i. e.* such that  $h\nu = mv^2/2 + W$ ) is proportional to the cube of the wave-length and to the square of the energy of binding, provided that the wave-length is short enough to eject the electron. The writer believes that this way of interpreting the experimental results may have importance from the theoretical point of view. It seems as though the X-ray quantum possesses an affinity for the electron which increases as the binding energy increases. It would seem then that the chance of an X-ray quantum giving up its entire energy to an electron in an electron vapour would be zero, since in this case there would be no binding energy. Hence there is probably no photoelectric effect in an electron vapour. In such a vapour the X-ray quantum should only be scattered. This scattering would take place with change of wave-length of the scattered quantum, part of the energy of the original quantum going into the production of a "recoil" electron as shown by A. H. Compton ‡. The writer has recently published a Corpuscular Quantum Theory of the Scattering

\* S. J. M. Allen, Phys. Rev. xxiii. p. 291 (1924).

† Warburton and Richtmeyer, Phys. Rev. xxiii. p. 291 (1924).

‡ A. H. Compton, Phys. Rev. xxi. p. 483 (1923).

of X-rays \*, and has shown in a recent letter to 'Nature' † that if an electron has a radius of  $4.57 \times 10^{-13}$  cm., and if the X-rays are supposed to be corpuscles which are scattered when they hit an electron, the mass scattering coefficient would be  $0.2 \text{ gram}^{-1}$ , which is very nearly that found experimentally. It seems that the photoelectric effect of X-rays is altogether a different process from the scattering of X-rays, as all the collisions of the X-ray corpuscles with electrons are accounted for by the observed value of the scattering coefficient. It seems possible that the photoelectric effect takes place only when the X-ray quantum or corpuscle passes between the electron and the nucleus. In fact it seems that the presence of the nucleus is a necessary factor in the photoelectric effect. It is interesting to speculate as to why it is that on the quantum passing between the electron and the nucleus the chance of the electron being ejected varies as the square of the binding energy. Bubb ‡ in a recent letter to 'Nature,' introduces the idea of a vector quantum. He speaks of the quantum "exploding" in a direction perpendicular to its line of flight. In his view the nucleus provides the seat of the reaction when the electron is ejected.

It would be very interesting to test whether anything like the empirical law proposed in this paper holds in the case of light. It is perhaps worth while noting that Hughes and Klein § have shown that the chance of ionization per collision increases as the binding energy decreases for helium, neon, and argon, if the speed of the ionizing electron is kept constant. This implies that the chance of an electron being ejected by collision with another electron increases as the binding energy decreases and in this way varies in the opposite direction to that when the electrons are ejected photoelectrically by X-rays.

Washington University,  
St. Louis, Mo., U.S.A.  
March 22, 1924.

\* G. E. M. Jauncey, *Phys. Rev.* xxii. p. 233 (1923), and xxiii. p. 313 (1924).

† G. E. M. Jauncey, 'Nature,' cxiii. p. 196 (1924).

‡ F. W. Bubb, 'Nature,' cxiii. p. 237 (1924).

§ Hughes and Klein, *Phys. Rev.*, in print.

IX. *On the Collision of Spherical Bodies of Unequal Diameters and Densities at Very Low Velocities.* By D. B. DEODHAR, M.Sc., Reader in Physics, Lucknow University, Lucknow, India\*.

*Introduction.*

ASSUMING certain conditions, Hertz† has given an interesting discussion about the phenomena which occur when two balls impinge on each other. He has found out that the radius of the circle of pressure, which is the boundary of the surface of contact, varies as the  $\frac{3}{2}$  power of the radius of the impinging sphere, and that the duration of impact, that is the time during which the bodies are in contact, is very large compared with the gravest period of vibration of either of the balls. Schneebeli‡, Lafay§, and Northrup|| have done some work to compare experimentally the theory of impact put forth by Hertz. In all the cases investigated by these workers they found that their experimental results were not in agreement with the theoretical deductions.

It is well known that the total kinetic energy before impact cannot be equal to that after impact unless the impact is perfectly elastic; in all other cases there will be dissipation of energy in various forms. Hertz has shown that the maximum pressure increases with the relative velocity, being proportional to the  $\frac{2}{5}$  power of the velocity; while it is independent of the size of the balls. And the greater the velocity the more will the pressure exceed the elastic limit, and there will be a dissipation of energy. This dissipation was not contemplated by Hertz. Lord Rayleigh¶ did some work on the impact of balls, and showed that the proportion of translational energy transferred into the energy of vibration is very small. The dissipation of energy due to sound has been discussed by Banerji\*\*, who has shown that the sound produced by the impact of spheres is due to the impulse communicated to the atmosphere by the sudden reversal of the motion of the spheres. The dissipation of the energy may largely be

\* Communicated by the Author.

† Hertz. 'Miscellaneous Papers' (English translation), pp. 146-147.

‡ *Rep. d. Phys.* xxii. (1886).

§ *Comptes Rendus*, 1900.

|| *Frank. Inst. Jour.* 1911.

¶ *Phil. Mag.* xi. p. 283 (1906).

\*\* *Phil. Mag.* July 1916, Jan. 1918.

ascribed to the failure of the condition of perfect elasticity during impact. When we know that even small spheres travelling with a speed as low as one centimetre per second develop a pressure which is far greater than what perfect elastic conditions would allow, the dissipation of energy must inevitably result; and if the bodies be plastic a great deformation in the area of contact can be easily noticed. Again, it should also be expected that the relationship between the velocities of impinging bodies before and after impact, namely the coefficient of restitution, must vary in value, becoming less and less as the relative velocity increases. This has been observed recently by Vincent\*. Similarly, if the velocity of approach be made very small, the coefficient of restitution should increase and tend towards unity. Very recently Raman† has made observations upon impact of bodies at very low velocities, and has shown for two or three kinds of materials that the coefficient of restitution does really approach unity. In all his experiments Raman worked with balls of the same material and equal diameters. The present author thought it worth while to make experimental investigations as to how the coefficient of restitution is affected if the impinging balls be of different materials and unequal diameters; it was also thought interesting to find the influence of the change in the medium in which the balls were colliding.

#### *Experimental Technique.*

Experimental arrangements were in essentials the same as those of Raman‡; and as the observations were to be made for very low velocities, the relative velocities were recorded and measured by a photographic method. In order to obtain a slow and steady motion, the balls were suspended by a bifilar suspension in such a way that their height was eighteen feet from the ceiling. A horizontal slit was illuminated by a Pointolite lamp of one hundred candle-power through a condensing lens, and the image of this slit was focussed by a convergent lens on the point of contact of the two balls. Consequently no light could be seen on the other side of the balls unless they were held apart. This image was further focussed upon the slit of the camera by an additional convex lens suitably placed. A metre scale placed horizontally behind the balls ensured that on being released they fell through equal distances. A very small

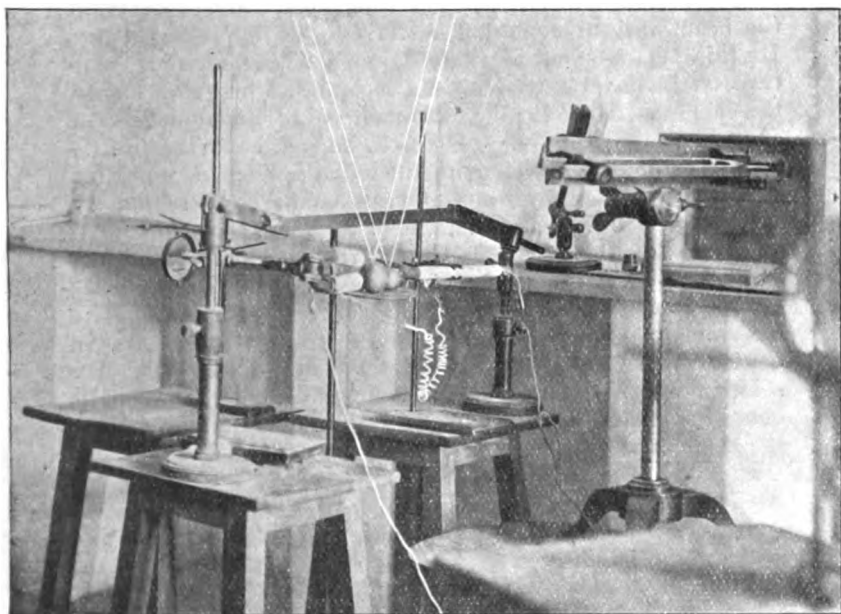
\* Camb. Phil. Soc. Proc. 1900.

† Phys. Rev. vol. xii. (1918).

‡ Phys. Rev. vol. xii. (1918).

- and light iron piece was attached to the remote side of each of the balls, and two small electromagnets were arranged so that on closing the circuit the balls could be held apart through any required distance, and on breaking the circuit they could approach each other and collide. (See photograph of the arrangement in fig. 1.) The camera consisted of a closed long wooden box, on the back of which a photographic plate is made to slide vertically downwards.

Fig. 1.



through a side groove. The motion of the photographic plate is regulated by means of a lead counterweight attached to the end of a string passing over a frictionless pulley. By properly adjusting the counterweight, the plate can be dragged up slowly and fairly uniformly past the slit. The switch controlling the electromagnets is so arranged that the experimenter can allow the counterweight to fall and then break off the current in such a way that the approach and rebounding of the balls take place while the photographic plate is moving past the slit of the camera. In this way two wedges of light are produced on the photographic plate corresponding to approach and rebound. The

gap between these wedges indicates the duration of impact—that is, the time during which the balls were in contact with each other. The ratio between the widths of the wedges measured at equal distances from the apexes is obviously equal to “ $e$ ,” the coefficient of restitution. In order to have a time-scale in these measurements, a large tuning-fork of 70 vibrations per second was mounted in front of the camera in such a way that a beam of light proceeding from another Pointolite lamp and made converging by means of a fine circular aperture and a lens, and reflected from a light mirror attached to the prong of this fork, did not obstruct the beam of light coming direct from the impinging balls. By this arrangement a reflected image of the circular aperture could be produced upon a second slit provided for in the camera. Thus the vibration curves of the tuning-fork, as well as the light wedges due to impact, could be simultaneously photographed upon the same plate; and duration of impact and other time-intervals could be measured by referring to the vibration curves of the fork.

For taking observations on the impact in water, the impinging balls were immersed in a glass basin of water placed on the top of a screw-motion table. The current in the electromagnets was adjusted so as to keep the balls in contact with the sides of the basin containing water. By selecting basins of larger or smaller diameters, the balls could be made to fall through any desired distance.

### *Observations and Discussion.*

Experiments were carried out with wooden and brass balls, which were specially turned in the laboratory workshop; the wood selected was the best Indian Shisham (sp. gr. = 1.13), which could sink in water. The wooden balls were 1.75 in. in diameter, while the brass balls were 2 in. and 1.5 in. in diameter respectively. The surfaces of these balls were polished to an equal extent as far as possible. After each impact, the surfaces taking part in actual collision were inspected to see if there was any permanent deformation in the way of small indentations; but nothing of the kind was detected for any of the sets of observations made. All the observations show that when the velocities are made extremely small, the coefficient of restitution rapidly tends to approach the value unity and actually becomes equal to 1, in all cases irrespective of any change either in the material of the colliding balls or in their diameters. It appears that Hodg-

kinson's \* formula for the coefficient of restitution between two dissimilar bodies, which is

$$e_{AB} = \frac{e_{AA}/q_1 + e_{BB}/q_2}{1/q_1 + 1/q_2}$$

(where  $e_{AB}$ =coefficient of restitution between the bodies A and B, and  $q_1, q_2$  are Young's moduli for the two bodies), does not hold good when the velocities are extremely small. The duration of impact appears to be greater than what is to be expected from the theory put forth by Hertz. According to Hertz †, the duration of impact for two spheres of equal radii and equal density is given by the relation

$$T = 2.9432 R \sqrt[5]{\frac{25\pi^2 s^2 (1-\sigma^2)^2}{8(V-U)q^2}},$$

where  $R$ =radius of sphere,  $s$ =density of the material,  $V$ =velocity of approach of one sphere,  $U$ =velocity of the second sphere,  $q$  and  $\sigma$  are Young's modulus and Poisson's ratio for the substance of which the spheres are made. At small velocities the duration of impact was observed to be independent of the diameters and materials of the spheres; and what is more interesting to note is that, other conditions being the same, the duration is greater in water than in air. This has been found invariably for all observations. The duration of impact could be very well measured by comparing the gap between the wedges of light on the photographic negative with the vibration curve of the tuning-fork. It appears that the general formula for the duration of impact should be modified by introducing an additional term corresponding to the density of the medium to account for the larger duration of impact in water. The results of several observations are given below in a graphical form. Figures 2 *a* and 2 *b* represent the case of brass balls 1.5 in. in diameter impinging in air and water respectively, while diagrams 3 *a*, 3 *b* and 4 *a*, 4 *b* represent respectively the cases of wood and brass, and brass balls of unequal diameters. In all these figures the coefficient of restitution is shown along the axis of  $Y$ , and the velocity of impact is plotted along the axis of  $X$ .

\* British Association Reports, 1834.

† 'Miscellaneous Papers' (English translation).



All these figures show that when the velocities are made extremely small there is practically no effect due to variation in diameter and material upon the change in the value of the coefficient of restitution. It appears that, in addition to the dissipation of energy in sound and heat in the act of collision, there must be dissipation of energy in some kind

Brass Balls: 1.5 in. diameter each.

Fig. 2 a.—Air.

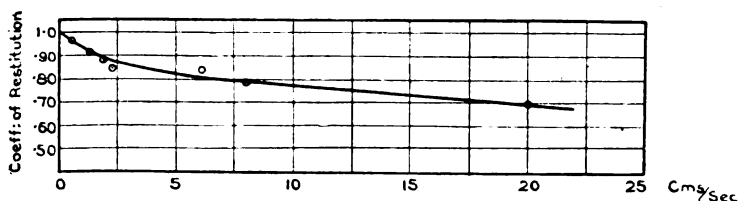
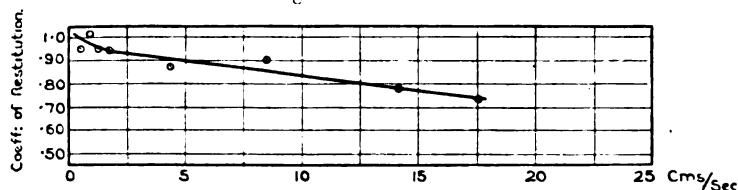


Fig. 2 b.—Water.



Brass Balls: 1.5 and 2.0 in. diameter.

Fig. 3 a.—Air.

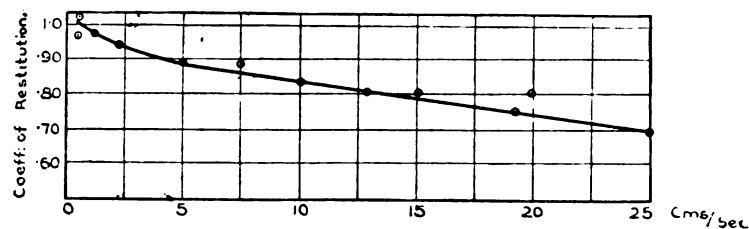
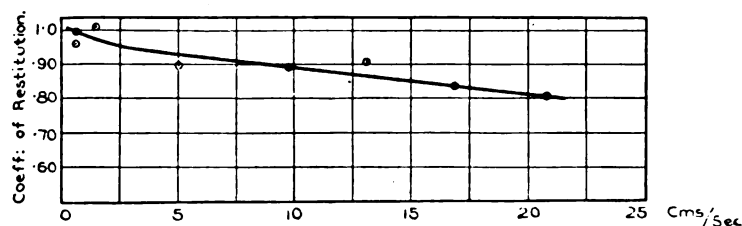


Fig. 3 b.—Water.



Wooden Ball: 1.75 in. diam. and Brass Ball: 1.5 in. diam.

Fig. 4a.—Air.

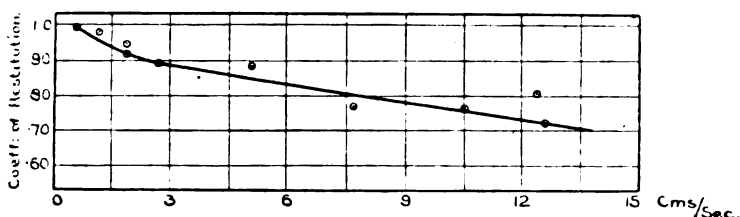


Fig. 4b.—Water.



of displacement of the molecules in the surface-layer of the ball-material, owing to which the coefficient of restitution increases when the velocity is decreased, and diminishes when the velocity is increased. Since, according to Hertz, it is known that the pressure exerted upon ordinary spheres of one-inch radius colliding with a velocity of 1 cm. per second and also the simultaneous maximum pressure at the centre of impact per unit area is 73 kilograms/mm.<sup>2</sup>, this pressure should produce deformation sufficiently great to be easily detected; but no such deformation was visible in the cases observed.

Now the question arises as to what happens to such an immense energy developed in the act of collision. Sound, heat, deformation, and vibration of the balls as a whole appear to be the different forms in which the energy dissipates itself. But remembering that the amount of sound energy produced is due to the reacting impulse given to the surrounding medium, and knowing that a small temperature change in the body is not enough to account for the whole energy-loss, one is inclined to think that very probably a portion of the stresses produced in the act of collision is spent in displacing the molecules in the surface-layer of the impinging balls; and that the change in the coefficient of restitution is due to such a surface change. This displacement becomes very minute when the velocity of approach is minimal, and it is only in this extreme case that the values

of the kinetic energy before and after impact are exactly equal to each other. Therefore, in all cases of collisions except those where the velocities are extremely small so as to make  $e=1$ ; the coefficient of restitution should play a great part in the dissipation of energy.

Thinking that it would be interesting to make microscopic observations of the surfaces of impinging bodies when the velocities are so small as not to show any apparent deformation, arrangement was made to take photomicrographs of these surfaces. In two or three cases which were thus observed it was distinctly seen that the photographs of surfaces after impact differed much from those before impact. But with a view to arrive at a decisive conclusion regarding my surface-layer hypothesis, it is hoped to conduct further scrutinizing observations after introducing more refinements in the experimental conditions. The problem is certainly most interesting, but at the same time extremely difficult, as the original surface may be disturbed owing to oxidation as well as during the very process of polishing.

*Summary.*

1. This paper deals with impacts of spherical balls of unequal diameters and densities investigated at very low speeds.
2. Impacts are taken in air as well as in water, and the manner in which the coefficient of restitution changes is studied photographically.
3. It is found that when the velocities are extremely small, changes in diameters and densities as well as a change in the medium in which collision takes place do not produce any appreciable effect upon the coefficient of restitution.
4. The duration of impact in water is invariably larger than that in air, and this fact calls for a modification in Hertz's duration formula.
5. It appears that during the process of impact molecular displacement takes place in the surface-layer, and that the coefficient of restitution is connected with dissipation of energy.
6. It is hoped to continue the photomicrographic study further by introducing additional refinements in the experimental conditions.

In conclusion the author takes this opportunity to express his best thanks to Professor Dr. Wali Mohammad, of the University, for his very helpful and encouraging suggestions during the progress of the work.

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X. *Wave-Power Transmission.* By E. A. BARCLAY-SMITH,  
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THE Constantinesco system of wave-power transmission has been successfully applied to the synchronization of the firing of machine-gun bullets from an aeroplane and to the Dorman Long boring machine.

In his book 'Sonics' the inventor investigates this form of power transmission by means of the "j" method. By this method he is enabled to take leakage and friction into account. He obtains a series of equations which show remarkable similarity to those found in the investigation of long-distance telephone-lines.

The following is an attempt to expound the phenomena occurring in wave-power transmission and to formulate an easy method of investigating them from first principles. Furthermore, an indication is given of the line of investigation to be followed when the data are such as will be met with in practice.

The essential feature of wave-power transmission is that power is transmitted to a distance by means of a fluid contained in a pipe. Pressure-waves are generated in the fluid at one end of the pipe by means of a reciprocating plunger. The plunger is operated by a crank or its equivalent, with the result that its motion is not simple-harmonic. As in most cases, however, the length of the connecting rod is great in comparison with the length of the crank, the plunger may be considered without appreciable error to have simple-harmonic motion.

At the other end of the pipe power is transmitted to a similar plunger by the pressure-waves in the liquid. The pipe may have several branches with a plunger at the end of each, in order that power may be received by several different machines.

In the event of any machine being out of use and thus not requiring any power, it may be disconnected from its plunger which will then be left to reciprocate without absorbing power (neglecting frictional losses), or the plunger may be locked. Every plunger will of course be provided with a flywheel or other arrangement to carry it over the dead points.

It is first necessary to investigate the happenings in a single pipe full of fluid when a plunger starts to reciprocate at one end.

\* Communicated by Prof. G. B. Jeffery, M.A., D.Sc.

*Phil. Mag. S. 6. Vol. 48. No. 283. July 1924.*

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In the following consideration the effects of friction and leakage in the pipe are neglected \*. The pressures referred to in this paper are those in excess of the pressure due to the static head of fluid necessary to keep the pipe full and to prevent cavitation taking place.

Let  $p$  = the instantaneous fluid pressure in lb. per sq. inch.

$K$  = coefficient of compressibility of the fluid in lb. per sq. inch †.

$\rho$  = density of the fluid in lb. per cubic inch.

$v$  = particle velocity in ins. per second.

$g$  = acceleration due to gravity in ins. per sec. per sec.

From a consideration of the motion of a particle of the fluid in the pipe it can easily be shown that if a single pressure-wave be travelling along a pipe it travels with velocity

$$\sqrt{\frac{Kg}{\rho}} \text{ ins. per second,}$$

and that

$$p = \sqrt{\frac{K\rho}{g}} \times v,$$

where  $v$  is the instantaneous velocity of the particles of the fluid in the direction in which the wave is travelling.

When the pressure-wave meets an obstruction part of it may continue to advance through the obstruction and thence be transmitted to a machine or to a continuum of the fluid on the further side, part of it will be reflected backwards as another pressure-wave not necessarily in phase with the original wave. This reflected wave when it reaches the generator will again be reflected in part, and this process will go on indefinitely.

Accompanying each of these pressure-waves will be a similar wave of particle velocity; the shape of the velocity-wave will be similar to the pressure-wave and at every point will obey the law

$$p = \sqrt{\frac{K\rho}{g}} \times v.$$

It is important to remember that the direction of the particle velocity corresponds with that in which the wave is travelling.

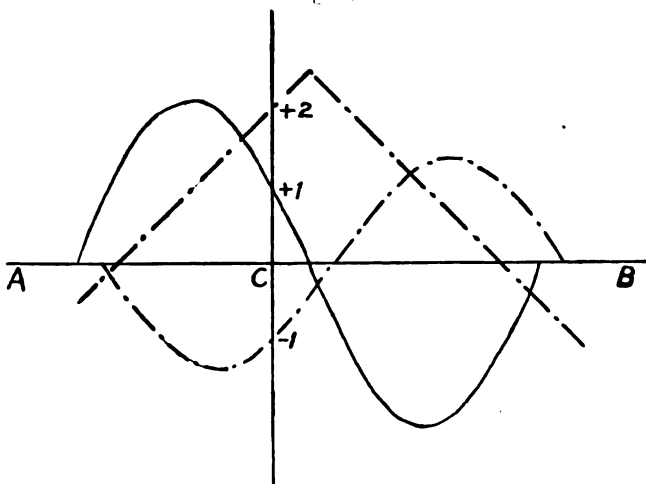
\* For a full consideration of their effects *vide* 'Sonics,' p. 46 *et seq.*

† In most cases the effect of expansion of the pipe need not be considered. Its effect would be slightly to alter the apparent value of  $K$ .

Thus when the plunger starts to reciprocate there will be created in the pipe a series of pressure-waves each accompanied by its corresponding particle-velocity wave and travelling to and fro along the pipe.

At any given point at any given instant of time the pressure is equal to the *sum* of the pressures due to the pressure-waves passing that point at that instant. The particle velocity, however, is in each case \* in the direction in which the wave is travelling; thus the direction of the particle velocities due to waves travelling in one direction is opposite to the direction of the particle velocities due to waves travelling in the reverse direction. Hence the resultant particle velocity will be equal to the *difference* between the sum of the velocities due to the velocity-waves travelling in one direction and the sum of the velocities due to the velocity-waves travelling in the opposite direction.

Fig. 1.

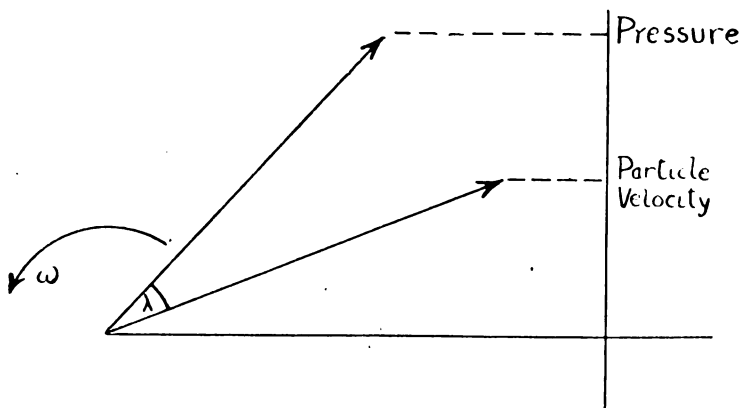


Thus if in fig. 1 the chain dotted lines represent two pressure-waves travelling along the pipe in the direction AB and the continuous line represents one travelling in the direction BA at the moment under consideration, the pressure at C will be equal to  $(2 - 1 + 1)$  lb. per sq. in., while the particle velocity will be equal to  $(2 - 1 - 1) \times \sqrt{\frac{g}{K\rho}}$  ins./second, and it will be in the direction AB. This rule applies whatever the shapes of the waves.

\* I. e. "in the case of each separate individual wave."

If the waves are sinoidal and all of the same frequency, the waves in each direction can be added together to form a single sinoidal wave. The pressure at any point will vary sinoidally with time. The particle velocity at that point will also vary sinoidally with time but will not necessarily be in phase with the pressure. Hence the pressure and particle velocity at some particular point can be represented vectorially, *i. e.* the actual quantities of the pressure and particle velocities respectively are represented by the projections of their vectors as they rotate with angular velocity  $\omega$  (fig. 2); the wave period, that is the time of one complete oscillation of the generator plunger, being  $\frac{2\pi}{\omega}$ .

Fig. 2.



If the vectors representing the pressure and the particle velocity at any given point are known, it is possible to analyse them into two sinoidal waves travelling in opposite directions by the following construction.

At the point C (fig. 3) let  $\overline{OP}$  be the pressure vector and let  $\overline{OQ}$  be the vector for particle velocity in the direction AB. The length  $OQ$  is the actual particle velocity  $\times \sqrt{\frac{K\rho}{g}}$  to the same scale as  $OP$ .

Join  $PQ$  and bisect it at  $R$ .

Join  $OR$  and draw  $OS$  equal and parallel to  $QR$ .

Then  $OR$  will represent both the pressure and particle velocity of the component wave travelling in the direction AB, and  $\overline{OS}$  will represent the pressure and particle velocity

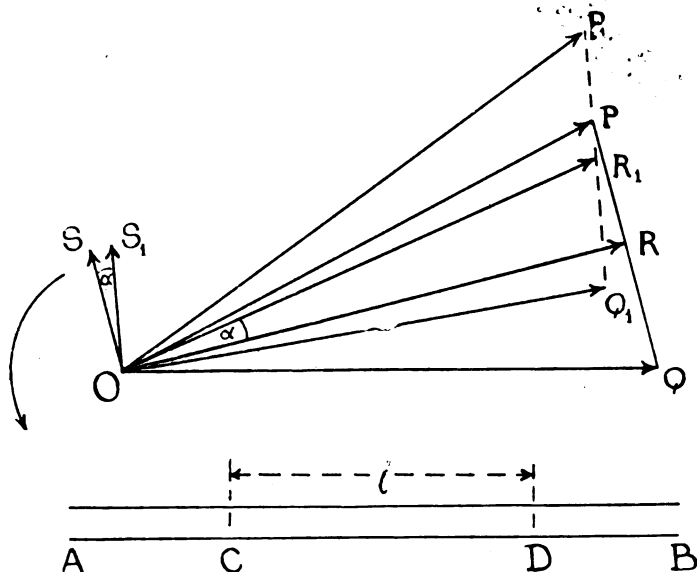
of the component wave travelling in the direction BA to the same scales as OP and OQ,

$$\text{since } \overline{OR} + \overline{OS} = \overline{OP}$$

$$\text{and } \overline{OR} - \overline{OS} = \overline{OQ}.$$

It must be remembered that the direction of the particle velocity represented by  $\overline{OR}$  is AB, while the direction of the particle velocity represented by  $\overline{OS}$  is BA.

Fig. 3.



Now the wave travelling in the direction AB reaches a point D distant  $l$  from C in  $l + \sqrt{\frac{Kg}{\rho}}$  seconds after it has reached C, while the wave travelling in the direction BA reaches D in  $l - \sqrt{\frac{Kg}{\rho}}$  seconds before it reaches C. Thus to find conditions at D it is necessary to turn the vector  $\overline{OR}$  forwards, i. e. counter-clockwise, through an angle  $\alpha$  and the vector  $\overline{OS}$  backwards, i. e. clockwise, through the same angle where

$$\alpha = \omega l \times \sqrt{\frac{\rho}{Kg}}.$$



Let  $OR_1$ ,  $OS_1$  be the new positions of the vectors  $\overline{OR}$ ,  $\overline{OS}$ . Then  $\overline{OP_1}$  the sum of  $OR_1$  and  $OS_1$  will represent the pressure at D, and  $\overline{OQ_1} = \overline{OR_1} - \overline{OS_1}$  will represent the particle velocity in the direction AB at D.

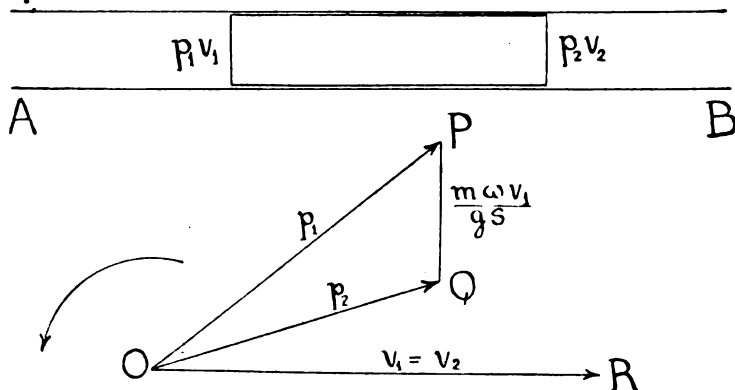
Thus if the conditions obtaining at any point are known those obtaining at any other point can be ascertained.

#### *Inertia and Hydraulic Capacities.*

An inertia acts as would a heavy metal cylinder placed in the pipe.

The particle velocity will be identical at either end of the inertia but the pressure at the two ends will differ since force must be supplied to give it the particle motion.

Fig. 4.

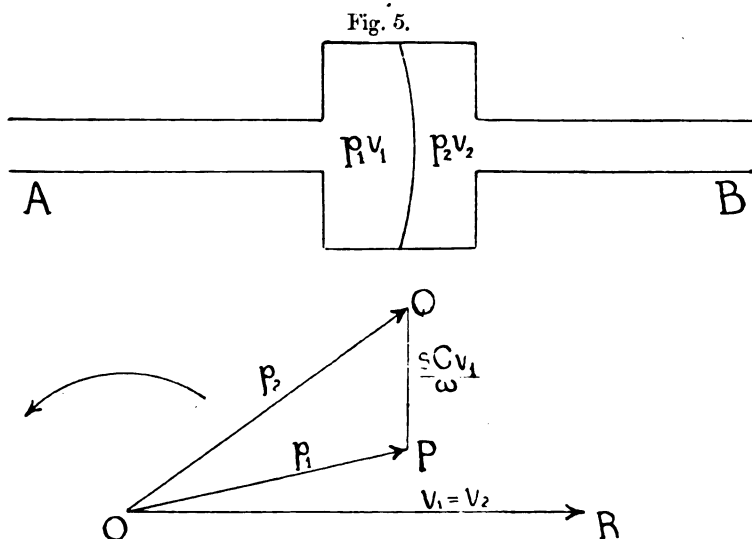


Let  $p_1, v_1$  be the pressure and particle velocity respectively at one end and  $p_2, v_2$  be the pressure and particle velocity respectively at the other end of the inertia, then  $v_1 = v_2$  in magnitude and phase. Let  $s$  be the sectional area of the pipe in square inches and  $m$  the mass of the inertia in lb. The maximum particle acceleration equals  $\omega \times$  the maximum particle velocity and the acceleration vector leads the velocity vector by  $90^\circ$ , both the particle acceleration and the particle velocity being considered to be in the same direction.

Thus if  $\overline{OR}$  (fig. 4) represents the particle velocity in the direction AB and  $\overline{OP}$  represents the pressure  $p_1$ , then  $\overline{OQ}$  will represent the pressure  $p_2$ , where  $\overline{QP}$  is perpendicular to  $\overline{OR}$  and represents  $\frac{m \omega v_1}{g s}$  the pressure required to give the inertia the particle motion.

Hydraulic capacities may be of two kinds :—(1) That which acts as would a rubber diaphragm placed in the pipe, where the difference of pressure on the two sides varies as the displacement. This form is sometimes termed a condenser. (2) That which acts as would a closed vessel containing gas placed in direct communication with the pipe, where the amount of fluid entering would vary directly as the amount of the pressure.

Taking case (1) and using the same notation as before,  $v_1 = v_2$  (fig. 5) in magnitude and phase; the maximum displacement  $= \frac{s}{\omega} \times$  the maximum particle velocity and the displacement vector lags  $90^\circ$  behind the velocity vector.



Thus if  $\overline{OR}$  (fig. 5) represents the particle velocity in the direction AB and  $\overline{OP}$  represents the pressure  $p_1$ , then  $\overline{OQ}$  will represent the pressure  $p_2$  where  $QP$  is perpendicular to  $OR$  and represents  $\frac{sCv_1}{\omega}$  where  $C$ , a constant for the condenser, is the difference in pressure in lb. per square inch caused by the displacement of one cubic inch of fluid.

It will be noticed that if a condenser is placed in close approximation to an inertia in the pipe, and

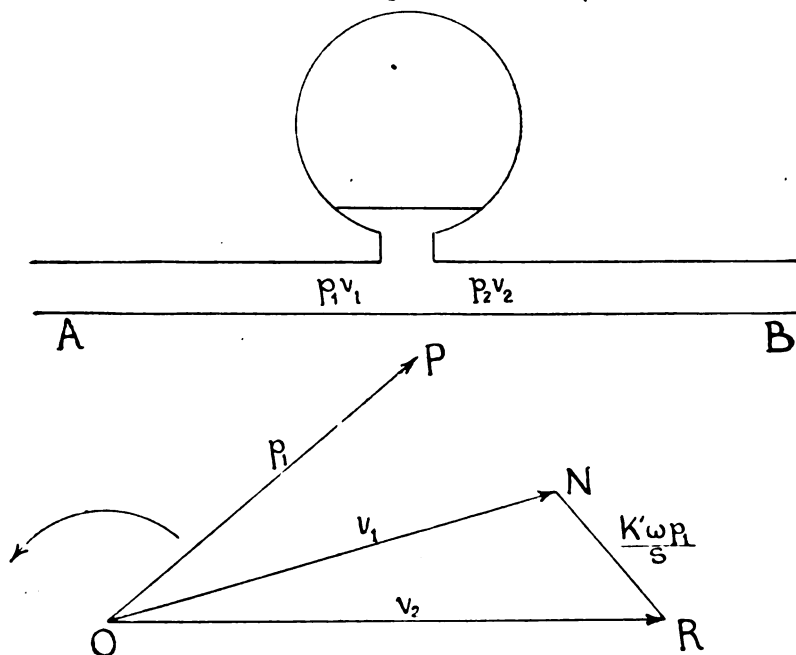
$$\frac{m\omega r_1}{sg} = \frac{sCv_1}{\omega} \quad \text{or} \quad \omega^2 = \frac{s^2C}{g},$$

the two effects neutralize one another.

Take case (2) using the same notation.

In this case  $p_1 = p_2$  (fig. 6) in magnitude and phase, but  $v_2$  differs from  $v_1$  by the differential of the amount of fluid entering the vessel divided by  $s$ . The amount of fluid entering the vessel  $= K'p_1$  cubic ins. where  $K'$ , a constant for the capacity, is equal to the number of cubic inches of fluid which will enter the vessel with an increase of pressure of 1 lb. per sq. inch; the differential of this amount will be  $K'\omega p_1$ , and in phase its vector will lead the pressure vector by  $90^\circ$ .

Fig. 6.



Thus if  $\overline{OP}$  (fig. 6) represents the pressure and  $\overline{ON}$  represents  $v_1$ , then  $\overline{OR}$  will represent  $v_2$  where  $RN$  is perpendicular to  $OP$  and represents  $\frac{K'\omega p_1}{s}$ , the particle velocities being considered to be in the direction  $AB$ .

From the above consideration it will be seen that if conditions at one point in the pipe are known it is possible to find conditions at another point in spite of the fact that an inertia or hydraulic capacity may intervene between them.

This may be done by the following process. In the first place find the component forward and backward waves at the known point, swing the vectors counter-clockwise or clockwise as the case may be through the angles necessary to find the conditions on the near side of the inertia or hydraulic capacity. The waves may now be combined and the conditions found on the far side by the addition to the pressure vector or to the velocity vector of the appropriate vector perpendicular to the velocity vector or to the pressure vector as the case may be. The conditions on the far side are to be analysed into forward and backward waves and the vectors representing the waves swung through the angle appropriate for the investigation of the conditions at the specified point. On recombining the waves the conditions required will be found.

### *Motors and Generators.*

Although there are many devices for starting motors from rest, every motor and generator in a wave-power transmission system is provided with a plunger reciprocating synchronously with the waves in the transmitting fluid. Two or more generators might be connected to the same pipe, but in such an arrangement their reciprocations must be synchronous. Several motors may receive power from the same pipe. The pipe may vary in size and may include inertias, condensers, and transformers, but in every case the pistons of the motors must reciprocate at the same rate as the pistons of the generators, though not necessarily in phase with them. It is assumed that the generators maintain a constant rate whatever the load.

The following data are available for determining the conditions at any point in the pipe. Since the piston displacement of the cylinders of each generator and motor are known, the particle velocities at the ends of the pipe can be calculated for any particular rate of oscillation. The power absorbed by each motor must be known since this can be varied at will. The simplest case, namely that of a generator and motor at either end of a uniform pipe, will now be considered.

Let AB be the pipe of length  $l$  having the generator at A and the motor at B. Three conditions may occur:—  
 (a) The piston of the motor may be fixed. (b) The piston of the motor may be oscillating but absorbing no power. (c) The motor may be absorbing power  $P$  inch-lb. per sec. Let  $p_A$ ,  $v_A$ ,  $p_B$ ,  $v_B$  be the pressures and particle velocities at

the generator and motor respectively;  $v_A$  and  $v_B$  both being in the direction AB.

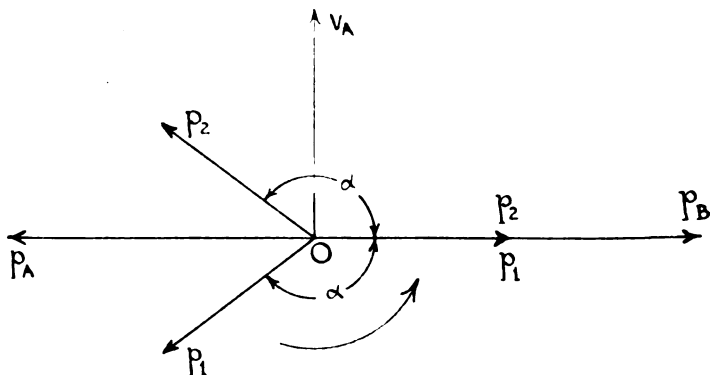
Then in every case  $v_A$  and  $v_B$  are known.

(a) In this case  $v_B = 0$ , hence the two component waves must be equal in magnitude and phase.

Let  $p_1$  (fig. 7) be the maximum pressure of the forward wave, and  $p_2$  that of the backward wave.

Then  $p_1 + p_2 = p_B$  and  $p_1 = p_2$ .

Fig. 7.



In order to find the conditions at the generator turn the vector representing the forward wave backwards, *i. e.* clock-wise, and the vector representing the backward wave forwards, *i. e.* counter-clockwise, in each case through an angle

$$\alpha = \omega l \times \sqrt{\frac{\rho}{Kg}},$$

the particle velocity at A will then be

$$2p_1 \sin \alpha \div \sqrt{\frac{Kg}{\rho}},$$

and this is known to be equal to  $v_A$ ,

$$\text{also} \quad p_A = 2p_1 \cos \alpha;$$

$$\text{thus} \quad p_B = v_A \operatorname{cosec} \alpha \sqrt{\frac{Kg}{\rho}} \quad \text{and} \quad p_A = v_A \cot \alpha \sqrt{\frac{Kg}{\rho}}.$$

It will be noticed that if  $\alpha$  is a multiple of  $\pi$ , that is

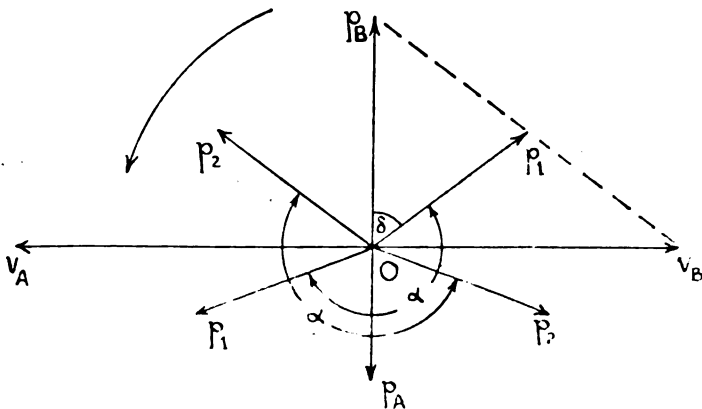
$$l = \frac{n\pi}{\omega} \sqrt{\frac{Kg}{\rho}},$$

the pressures at A and B would tend to become infinite.

The time of one oscillation  $= \frac{2\pi}{\omega}$  and the wave velocity  $= \sqrt{\frac{K}{\rho}}$ ; hence  $\frac{\pi}{\omega} \sqrt{\frac{K}{\rho}}$  = half a wave-length. Therefore if  $l$  is nearly equal to some multiple of half the wave-length, an inertia or hydraulic capacity must be inserted into the pipe in order to modify the conditions and thus prevent the bursting of the pipe.

(b) In this case  $v_B$  (fig. 8) is known, and as no power is absorbed the vector representing  $p_B$  must be at right angles to that representing  $v_B$ .

Fig. 8.



Analysing into component waves it will be found that  $p_1 = p_2$ . Let  $\delta$  be the angle at which  $p_1$  and  $p_2$  are inclined to  $p_B$ , as shown in fig. 8;

$$\text{then } 2p_1 \cos \delta = p_B \text{ and } 2p_1 \sin \delta = v_B \sqrt{\frac{K\rho}{g}} \dots (1)$$

Turning the vectors through the angle  $\alpha$  in order to find the conditions at A,

$$2p_1 \cos (\alpha + \delta) = p_A, \text{ and } 2p_1 \sin (\alpha + \delta) = v_A \sqrt{\frac{K\rho}{g}}, \quad (2)$$

combining with (1)

$$\frac{\sin (\alpha + \delta)}{\sin \delta} = \frac{v_A}{v_B}$$

$$\text{If } v_A = v_B, \quad \sin(\alpha + \delta) = \sin \delta,$$

$$\text{or} \quad (2n+1)\pi - (\alpha + \delta) = \delta,$$

$$\text{that is} \quad \delta = \left(\frac{2n+1}{2}\right)\pi - \frac{\alpha}{2},$$

$n$  being a whole number depending on the value of  $\alpha$ .

$$\therefore \quad 2p_1 = \frac{v_A}{\sin \frac{1}{2}\{(2n+1)\pi + \alpha\}} \sqrt{\frac{K\rho}{g}},$$

$$\text{and} \quad p_A = v_A \sqrt{\frac{K\rho}{g}} \cot \frac{1}{2}\{(2n+1)\pi + \alpha\},$$

$$p_B = v_A \sqrt{\frac{K\rho}{g}} \frac{\cos \frac{1}{2}\{(2n+1)\pi - \alpha\}}{\sin \frac{1}{2}\{(2n+1)\pi + \alpha\}}.$$

Thus if  $\alpha$  is equal to some odd multiple of  $\pi$ , or in other words if  $l$  is equal to some odd multiple of half the wavelength, the pressures tend to become infinite.

(c) A sinoidal pressure-wave travelling along a pipe is accompanied by a sinoidal particle velocity wave in phase with it of which the maximum value is  $p\sqrt{\frac{g}{K\rho}}$ , where  $p$  is the maximum value of the pressure. Hence the power transmitted by such a wave is  $\frac{p^2 s}{2} \sqrt{\frac{g}{K\rho}}$  if the sectional area of the pipe is  $s$  sq. inches.

In the case under consideration the motor is absorbing power at the rate of  $P$  inch-lb. per second.

Let the vectors  $\overline{Op_1}$ ,  $\overline{Op_2}$  (fig. 9) represent the forward and backward waves respectively as before. Let  $\theta$  be the angle by which  $\overline{Op_2}$  leads  $\overline{Op_1}$  at B. Then, since the backward wave carries power back to the generator, the power absorbed

$$= P = \frac{(p_1^2 - p_2^2)}{2} s \sqrt{\frac{g}{K\rho}} \dots \dots \dots (1)$$

$$\text{Also} \quad v_B^2 = p_1^2 + p_2^2 - 2p_1 p_2 \cos \theta. \dots \dots \dots (2)$$

On swinging the vectors backwards and forwards through the angle  $\alpha$  ( $= \omega l \sqrt{\frac{\rho}{Kg}}$ ) the equation

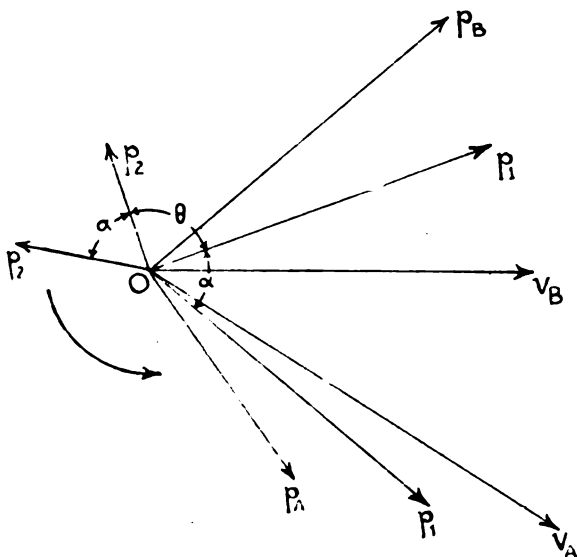
$$v_A^2 = p_1^2 + p_2^2 - 2p_1 p_2 \cos(\theta + 2\alpha) \dots \dots \dots (3)$$

is obtained. Hence there are three equations by means of which the three unknowns  $p_1$ ,  $p_2$ , and  $\theta$  can be determined.

It is to be noticed that as  $p_1$  and  $p_2$  are unequal there is no tendency for the pressure to become infinite whatever the value of  $\alpha$ .

With the addition of complications such as inertias or hydraulic capacities to the pipe line the investigation will naturally become more complex, but in every case equations equal in number to the unknowns can be obtained by the method set forth in this paper.

Fig. 9.



In the case where a pipe divides in order to supply two or more motors the line of investigation would be as follows. At each of the  $n$  motors there can be obtained two equations for the three unknowns  $p_1$ ,  $p_2$ , and  $\theta$ . If all the waves are transferred to the junction the composite pressures for each pipe at this point will be equal in magnitude and identical in phase; this fact will yield  $(n-1)$  equations. The particle velocity in the generator pipe will be equal to the vectorial sum of the particle velocities in the  $n$  motor pipes. By transferring the waves to the generator, the particle velocity at which is known, another equation can be obtained and this equation will complete the  $3n$  equations necessary to find the  $3n$  unknowns.

My grateful thanks are due to Professor G. B. Jeffery of King's College, London, for very valuable criticism.

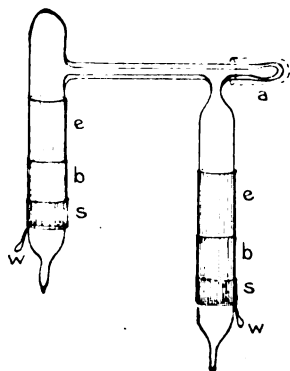


XI. *Modified Vacuum Tubes.* By J. J. MANLEY, M.A.,  
Research Fellow, Magdalen College, Oxford\*.

**D**URING the spectroscopic examination of small quantities of gas at very low pressures, two well-known defects of the vacuum tube were more than usually apparent. The two defects—(1) an insufficient luminosity for the feebler lines of spectra, and (2) contamination of the gas under examination by others emitted by the electrodes—were removed in the following way.

1. *Insufficient luminosity.*—From an end-on tube, light passes out in two equal portions which travel in opposite directions; hence 50 per cent. of the available light is, for spectroscopic work, ineffective. To avoid difficulties attending this great loss, the tube was altered and given the slightly

Fig. 1.



different form shown in fig. 1, and the limb *a* silvered to an extent represented by the enclosing dotted line. Under these circumstances, light which ordinarily emerges and becomes useless is reflected back, and so assists in illuminating the slit: thus the intensity is largely increased, and lines previously measured with difficulty are now so much enhanced in strength that their positions may be determined with ease. A further advantage is secured if, in addition to silvering the limb *a*, the capillary tube is treated as recommended by Merton and Johnson†. Maximum

\* Communicated by the Author.

† Phil. Mag. xlv. p. 448 (Sept. 1923).

intensity and uniformity of illumination are thus simultaneously realized.

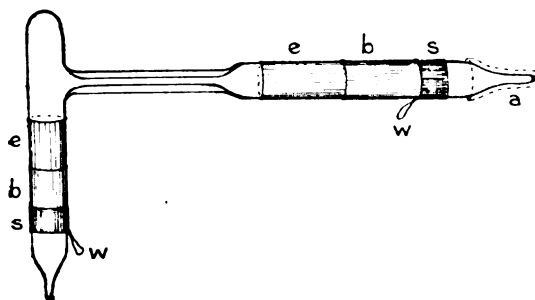
2. *Occluded Gases*.—The inconveniences arising from occluded gases were avoided by use of electrodes wholly external. This excellent plan, although not new, does not appear to be sufficiently well known or appreciated. Possibly this is because external electrodes as ordinarily attached are apt to lead to a piercing of the tube, and that within a comparatively short time. Numerous experiments have, however, led to the conclusion that by fulfilling two essential conditions, tubes having external electrodes are in every respect quite as reliable as others. The required conditions are (1) a certain massiveness for the electrodes, and (2) a complete absence of air-bubbles from the engaging surfaces of glass and electrode: these conditions may be secured in the following way.

First, the tube is chemically cleaned and dried both within and without. Next, that part of the discharge chamber upon which the electrode is to be built is thinly and evenly coated with concentrated and clear shellac varnish; then a strip of tin-foil 7 cm. wide and 20 cm. long is placed upon the varnish, with one of its ends parallel to the axis of the tube: the tube, held horizontally, is now slowly rotated so as to wind the foil; as the winding proceeds, the foil is gently and continuously rubbed in order to expel the enclosed air. When the foil covers some three-quarters of the circumference of the tube, the inner surface of the unwound portion is coated with varnish, and the winding and rubbing resumed and continued until all the foil has been attached to the tube: finally, the electrode *e* thus built up is varnished and, when dry, given a four-fold band *b* of tin-foil. At one end of this band, which is 3 or 4 cm. wide, is embedded a looped copper wire *w*, which serves as a connector for an induction coil. The band and its wire are tightly strapped to the electrode by two turns of adhesive tape *s*, and a last coat of varnish applied. An end-on vacuum tube silvered at *a* and fitted with external electrodes is represented in fig. 1. The tube is of "Duro" glass; its discharge chambers are 9 cm. long and 1.5 cm. wide. Tubes of this kind have for months been frequently used for prolonged periods; and although the coil operating the tubes yields a powerful 1-inch spark, in no instance has a tube broken down or become in any way visibly defective. Such tubes are made with ease, and the use of expensive platinum wire avoided.

3. *Some further simplifications*.—Two other modifications

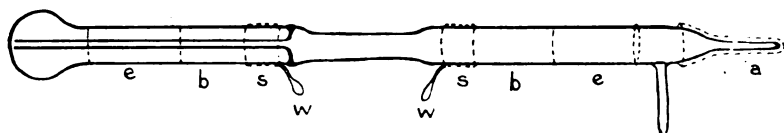
of the end-on tube are shown in figs. 2 and 3. That seen in fig. 2 involves the making of one T-joint only. It is more

Fig. 2.



efficient than that shown in fig. 1. The increased efficiency is due to the reflecting power of the inner surface of the tin-foil forming the external electrode of the horizontal chamber. Here, in a secondary degree, the tin-foil functions in much the same way as does the silvered surface of Merton and Johnson's tube (*vide supra*).

Fig. 3.



The efficiency of the tube represented in fig. 3 is superior to that of the other two: the reason is threefold. (1) In this form the *whole* glow is viewed end-on; (2) *both* electrodes now function after the manner of Merton and Johnson's silvered surface; and (3) the end of the capillary tube viewed by the spectroscope can be brought very close to the slit. In connexion with this last point, we observe that distortion must be absent from that portion of the bulb confronting the capillary tube. The desired uniformity may be obtained by re-forming the bulb some four or five times. The terminal limbs *a* of tubes 2 and 3 are, like that of tube 1, silvered to an extent indicated by the enveloping dotted lines. The letters appended to figs. 2 and 3 retain the meanings assigned in fig. 1.

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XII. *Monoplane Theory.*By N. K. Bose, *Ph.D.* (Göttingen) \*.

(1)

LET us suppose that there is an infinite volume of frictionless and incompressible fluid moving in an infinite space with a constant velocity  $V$  and that in this fluid we place a plane, the length of the plane being at right angles to the direction of the free fluid. Now what happens has been described by Prof. Prandtl in his paper "Tragflügeltheorie." It is known from simple experimental facts that to keep the aeroplane fixed in this moving fluid a certain force must be applied. Now whence comes this force which must have been applied by the fluid on the body as we have supposed the fluid to be frictionless and incompressible? To account for this fact Kutta assumed that there is a circulation of liquid round the aeroplane. From our conceptions of classical Hydrodynamics we know that circulation round a closed fluid line cannot change nor can it be generated by any known forces. The explanation of why, in spite of this, the aeroplane gained circulation is given by Prof. Prandtl as follows: At the first moment of the motion there is still no circulation, there is only a flow at high velocity around the trailing edge. This motion cannot however continue: there is instantly formed at the trailing edge a vortex of increasing intensity, which in accordance with a theorem of Helmholtz that the vortex is made up of the same fluid particles remains with the fluid as it passes on. The circulation round the wing and the vortex taken together remains equal to zero, there remains then round the wing a circulation equal and opposite to that of the vortex which has gone off with the current.

To give this idea a mathematical basis, what is necessary is to divide the aeroplane surface into so many "differential surfaces" so that each small elemental surface may be looked upon as an aeroplane on which fluid pressure is calculated independently of all other elements, and then it is integrated throughout the whole volume occupied by these elemental aeroplanes. The conception is something like this: at each elemental aeroplane there is a circulation which is denoted by  $\gamma$ , and from the edges of this element vortices flow off with the fluid; the strength of the elemental vortices is  $\epsilon$ . So we can picture the thing like this: under each differential aeroplane there is a vortex of strength  $\gamma$  which is fixed with

\* Communicated by Prof. C. Runge, the University of Göttingen.  
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the element and from each element a vortex line is flowing off with the liquid whose strength per unit volume is  $\epsilon$ , so that the aeroplane becomes the seat of innumerable fixed vortices of strength  $\gamma$  per unit volume, and from the aeroplane free vortices are flowing off with the liquid like ribbons with strength  $\epsilon$  per unit volume.

With this conception Prof. Prandtl finds the force on each differential surface as  $\rho(\gamma \times \mathfrak{B})$  per unit volume, where  $\rho$  is the density of the fluid,  $\gamma$  is the vortex strength at that element, and  $\mathfrak{B}$  is the velocity of the liquid at that element, so that the force with which the aeroplane must be held to keep it fixed is given by

$$K = \rho \iiint (\gamma \times \mathfrak{B}) dx dy dz,$$

where the integration is throughout the whole volume filled by the vortices.

Now let us suppose that the bound vortices give rise to a velocity  $V_1$  in the liquid, and the free vortices  $\epsilon$  to  $V_2$ , so that

$$\mathfrak{B} = V + V_1 + V_2 = V + V^*,$$

so that  $V^*$  is the velocity superimposed on the free fluid due to the presence of the aeroplane with its vortices. Since  $\gamma + \epsilon$  gives rise to the velocity  $V^*$ , then

$$\gamma + \epsilon = \text{curl } V^* = \nabla \times V^* ;$$

also we know that  $V$  is constant, so

$$\nabla \times V = 0 ;$$

and since the free vortices are flowing off with the liquid so that the axis of  $\epsilon$  is always parallel to  $\mathfrak{B}$ ,

$$\epsilon \times \mathfrak{B} = 0 \quad \text{or} \quad (\nabla \times V_2) \times \mathfrak{B} = 0,$$

so that

$$\begin{aligned} K &= \rho \iiint (\gamma \times \mathfrak{B}) dx dy dz \\ &= \rho \iiint (\nabla \times V_1) \times (V + V^*) dx dy dz \\ &= \rho \iiint (\nabla \times V^*) \times (V + V^*) dx dy dz \\ &\quad \text{since } (\nabla \times V_2) \times \mathfrak{B} = 0, \\ &= \rho \iiint (\nabla \times V^*) \times V dx dy dz + \rho \iiint (\nabla \times V^*) \\ &\quad \times V^* dx dy dz. \end{aligned}$$

Now the first integral can be written

$$\rho \left\{ \iiint (\nabla \times V^*) dx dy dz \right\} \times V = \rho(\Gamma + E) \times V^*,$$

where  $\Gamma$  and  $E$  are single equivalent vortices that can replace the bound and the free vortices respectively for all purposes.

For the second integral

$$I = \iiint (\nabla \times V^*) \times V^* dx dy dz$$

we have from properties of Vector analysis

$$\begin{aligned} (\nabla \times V^*) \times V^* &= -V^* \times (\nabla \times V^*) \\ &= -(V^* \cdot \nabla)V^* + (V^* \cdot \nabla)V^* \\ &= (V^* \cdot \nabla)V^* - \frac{1}{2}\nabla(V^* \cdot V^*). \end{aligned}$$

If  $u^*, v^*, w^*$  be the components of  $V^*$  along the three coordinate axes and  $i, j, k$  be three unit vectors along these axes, then

$$\begin{aligned} (\nabla \times V^*) \times V^* &= \left( u^* \frac{\partial u^*}{\partial x} + v^* \frac{\partial u^*}{\partial y} + w^* \frac{\partial u^*}{\partial z} \right) i \\ &\quad + \left( u^* \frac{\partial v^*}{\partial x} + v^* \frac{\partial v^*}{\partial y} + w^* \frac{\partial v^*}{\partial z} \right) j \\ &\quad + \left( u^* \frac{\partial w^*}{\partial x} + v^* \frac{\partial w^*}{\partial y} + w^* \frac{\partial w^*}{\partial z} \right) k - \frac{1}{2}\nabla(q^{*2}), \end{aligned}$$

where  $q^*$  is the scalar value of  $V^*$ .

Hence

$$\begin{aligned} I &= i \iiint \left( u^* \frac{\partial u^*}{\partial x} + v^* \frac{\partial u^*}{\partial y} + w^* \frac{\partial u^*}{\partial z} \right) dx dy dz \\ &\quad + j \iiint \left( u^* \frac{\partial v^*}{\partial x} + v^* \frac{\partial v^*}{\partial y} + w^* \frac{\partial v^*}{\partial z} \right) dx dy dz \\ &\quad + k \iiint \left( u^* \frac{\partial w^*}{\partial x} + v^* \frac{\partial w^*}{\partial y} + w^* \frac{\partial w^*}{\partial z} \right) dx dy dz \\ &\quad - \frac{1}{2} \iiint \nabla(q^{*2}) dx dy dz. \end{aligned}$$

Now to integrate

$$\begin{aligned} & \iiint \left( u^* \frac{\partial u^*}{\partial x} + v^* \frac{\partial u^*}{\partial y} + w^* \frac{\partial u^*}{\partial z} \right) dx dy dz \\ &= \iiint u^* \frac{\partial u^*}{\partial x} dx dy dz \\ & \quad + \iiint v^* \frac{\partial u^*}{\partial y} dy dz dx + \iiint w^* \frac{\partial u^*}{\partial z} dz dx dy. \end{aligned}$$

Integrating by parts

$$\begin{aligned} &= \iint \left\{ u^* u^* - \int u^* \frac{\partial u^*}{\partial x} dx \right\} dy dz \\ & \quad + \iint \left\{ u^* v^* - \int u^* \frac{\partial v^*}{\partial y} dy \right\} dz dx \\ & \quad + \iint \left\{ w^* u^* - \int u^* \frac{\partial w^*}{\partial z} dz \right\} dx dy. \end{aligned}$$

Now if we conceive of a surface  $dS$  at  $(x, y, z)$ , if  $l, m, n$  be the direction cosines of its normal,

$$dy dz = l dS, \quad dz dx = m dS, \quad dx dy = n dS,$$

so that

$$\begin{aligned} & \iiint \left( u^* \frac{\partial u^*}{\partial x} + v^* \frac{\partial u^*}{\partial y} + w^* \frac{\partial u^*}{\partial z} \right) dx dy dz \\ &= \iint (lu^* + mv^* + nw^*) u^* dS \\ & \quad - \iiint \left( \frac{\partial u^*}{\partial x} + \frac{\partial v^*}{\partial y} + \frac{\partial w^*}{\partial z} \right) u^* dz dy dx. \end{aligned}$$

Now

$$\frac{\partial u^*}{\partial x} + \frac{\partial v^*}{\partial y} + \frac{\partial w^*}{\partial z} = 0,$$

as the liquid is homogeneous and incompressible.

Hence

$$\begin{aligned} I &= \iint (lu^* + mv^* + nw^*) (u^* i + v^* j + w^* k) dS \\ & \quad - \frac{1}{2} \iiint \nabla(q^{*2}) dx dy dz \\ &= \iint (lu^* + mv^* + nw^*) \mathbf{V}^* dS \\ & \quad - \frac{1}{2} \iiint \nabla(q^{*2}) dx dy dz, \end{aligned}$$

where the surface integral is over a surface enclosing all the vortices and the volume integral throughout a space covered by the vortices.

Now  $\nabla(q^{*2}) = 2q^* \nabla(q^*),$

$$\begin{aligned} \therefore \iiint \nabla(q^{*2}) dx dy dz &= 2 \iiint q^* \nabla(q^*) dx dy dz \\ &= 2i \iiint q^* \frac{\partial q^*}{\partial x} dx dy dz + 2j \iiint q^* \frac{\partial q^*}{\partial y} dy dz dx \\ &\quad + 2k \iiint q^* \frac{\partial q^*}{\partial z} dz dx dy \\ &= i \iint l q^{*2} dS + j \iint m q^{*2} dS + k \iint n q^{*2} dS, \\ &= \iint (li + mj + nk) q^{*2} dS = \iint N q^{*2} dS, \end{aligned}$$

where  $N$  is the unit normal vector to the element of surface. So that

$$I = \iint (lu^* + mv^* + nw^*) V^* dS - \frac{1}{2} \iint N q^{*2} dS,$$

then

$$K = \rho(\Gamma + E) \times V + \rho \iint (lu^* + mv^* + nw^*) V^* dS - \frac{1}{2} \rho \iint N q^{*2} dS.$$

Now  $\Gamma$  is  $\Gamma l$  of the Kutta-Joukowski formula for lift, so that  $\rho(\Gamma \times V)$  is a force perpendicular to  $V$ , and according to Prof. Gibbs's conception if  $V$  be horizontal, from left to right, and  $\Gamma$  along the length of the aeroplane from behind forward, then the force is vertically downward, hence it is opposite to "lift," and equivalent in amount to it. The force  $\rho(E \times V)$  is also perpendicular to  $V$ , hence its component along  $V$  is zero, and it being of a higher order of small quantities than  $\rho(\Gamma \times V)$ , its effect on the latter force, *i. e.* the lift, is negligible. Hence to a first order of approximation

$$E \times V = 0.$$

Now the integral

$$\rho \iiint (\gamma \times \mathfrak{B}) dx dy dz$$

is to be integrated throughout the whole space covered by the vortices. But if we extend the limits of integration so as



to make them infinite we do not thereby change the value of the integral, because outside the space where the vortices are the value of the integrand is zero as at every point there  $\gamma=0$ . So we can take all the integrals over infinite space. For the surface integrals let us assume that we enclose the volume by a cylindrical surface and two parallel planes so that the axis of the cylinder is parallel to  $V$  and passes through the aeroplane and the two planes; one,  $A_1$ , is in front of the aeroplane and the other,  $A_2$ , is behind the aeroplane and they are perpendicular to the axis of the cylinder. If now we take the radius  $R$  of the cylinder very great, both the surface integrals would vanish over it since the velocities are of order  $\frac{1}{R^2}$  and  $dS$  of order  $R^2$ . Also the values of

these two surface integrals over  $A_1$  will vanish if we take  $A_1$  sufficiently far off from the aeroplane. As to the values of these integrals over  $A_2$ , we must remark that the velocities  $q^* V^* u^* v^* w^*$  are composed of two parts; one is due to the bound vortices and the other one to the free vortices, so that

$$q^* = q_1 + q_2, \quad V^* = V_1 + V_2, \quad u^* = u_1 + u_2, \\ v^* = v_1 + v_2, \quad w^* = w_1 + w_2.$$

Now we see that as we move the plane  $A_2$  further and further away from the aeroplane always parallel to itself, the quantities  $q^* V^* u^* v^* w^*$  approximate more and more to  $q_2 V_2 u_2 v_2 w_2$  and the influence of the bound vortices becomes feebler and feebler, so that ultimately when the plane  $A_2$  is far off enough from the aeroplane then we can take with sufficient degree of approximation

$$q^* = q_2, \quad V^* = V_2, \quad u^* = u_2, \quad v^* = v_2, \quad w^* = w_2,$$

and the surface integrals become

$$\rho \iint (lu_2 + mv_2 + nw_2) V_2 dS - \frac{1}{2} \rho N \iint q_2^2 dS.$$

Now  $lu_2 + mv_2 + nw_2$  is the component of the velocity due to the free vortices normal to  $A_2$ , but we have so taken the plane  $A_2$  that it is perpendicular to  $V$ , i. e. perpendicular to the direction of the vortices which are parallel to each other and to  $V$  when far off from the aeroplane, so that the normal components of the velocities generated by these free vortices are zero, i. e. the first of the above two integrals are zero.

Hence we get

$$K = \rho (I \times V) - \frac{1}{2} \rho N \iint q_2^2 dS.$$

Thus we see that to keep the aeroplane in position this force  $K$  must be applied on the aeroplane, which easily decomposes itself into two parts perpendicular to each other. Thus the air force on the aeroplane can be decomposed into two parts: one is what is called Lift and is equal to  $\rho(\Gamma \times V)$  and is perpendicular to  $V$  and upwards; whereas the other portion is what is called Drag and is equal to  $\frac{1}{2}\rho \iint q_2^2 dS$  and is parallel and in the same direction as  $V$ .

From this expression of drag it is at once apparent that drag is exactly equivalent to that portion of the energy which is flowing off with the liquid in the free vortices and will be ultimately dissipated into the air as heat. That the energy is exactly equivalent to the drag found by Prof. Prandtl will be shown afterwards. It may be of interest to note that the integral (11) in the "Tragflügeltheorie," which Prof. Prandtl has assumed to be zero only when the bound vortices are parallel to each other, can be shown to be always zero by means of the foregoing vector identity

$$(\nabla \times V) \times V = (V \cdot \nabla)V - \frac{1}{2}\nabla(V \cdot V),$$

and the (11) integral can be reduced to

$$\iiint (\nabla \times V_1) \times V_1 dx dy dz.$$

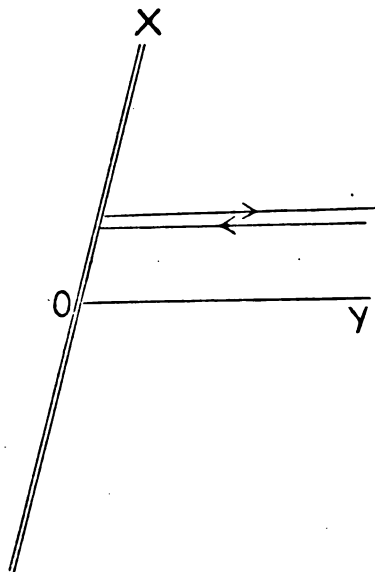
(2)

To find the velocity-potential and other characteristics of the vortex system that is flowing off with the liquid we shall have to refer again to another conception of Prof. Prandtl. He found that the density of the lift (lift per unit length) is not constant over the whole space of the aeroplane, but in general falls off gradually from a maximum at the middle to zero at the ends. In accordance with what has been proved there corresponds to this a circulation decreasing from within outwards. Therefore, according to the theorem that by the displacement of the closed curve the circulation  $\Gamma$  can only change if a corresponding quantity of vortex filaments are cut, we must assume that vortex filaments proceed off from the trailing edge wherever  $\Gamma$  changes. For a portion of this edge of length  $dx$ , the vortex strength that is flowing off is therefore to be written  $\frac{d\Gamma}{dx} dx$ , hence per unit length of the edge the strength of the free vortices is  $\frac{d\Gamma}{dx}$ . These vortex filaments flowing off, closely side by side, form

taken as a whole a surface-like figure which is known as "Vortex Sheet."

The strengths of our vortex sheet remain unchanged during the whole flight, yet the separate parts of the sheet influence each other and there takes place a gradual rolling up of the sheet. An exact theoretical investigation of this phenomenon has not been made yet; it can only be said that the two halves of the sheet become concentrated more and more, and finally at great distances from the wing there remain a pair of vortices with rather weak core. As a first approximation we shall not consider this latter development of the sheet, but shall proceed with the calculations as if all the vortex filaments were running off behind in straight lines opposite to the direction of flight.

Fig. 1.



Now to treat the subject mathematically we consider the vortex sheet as a plane, say  $x$ - $y$  plane, and take the axis of  $y$  parallel to the vortex filaments and the  $x$ -axis along the length of the aeroplane, and take the origin of coordinates  $O$  at the middle point of the aeroplane, so that on the positive side of the  $x$ -axis all the free vortices have a clockwise rotation when viewed along this direction of flight, and on the negative side of the  $x$ -axis a counter-clockwise rotation. Let

us take a vortex filament ABC of strength  $\frac{d\Gamma}{dx} dx$  at  $A(x, 0, 0)$  and find out  $\phi, \psi, u, v, w$  due to it at a point  $P(x', y', z')$  in the free liquid.

We know from the properties of a single straight vortex, on one side going to infinity and on the other side ending on a surface,

$$\psi = \frac{1 + \cos \alpha}{4\pi} \frac{d\Gamma}{dx} dx \log r$$

and

$$\phi = -\frac{1 + \cos \alpha}{4\pi} \frac{d\Gamma}{dx} dx \cdot \theta,$$

where  $\theta$  increases with the circulation due to the vortex filament and  $r$  the distance of P from the filament, and  $\alpha = \angle ABP$ .

$$\begin{aligned} \therefore w &= \phi + i\psi = i \frac{1 + \cos \alpha}{4\pi} \frac{d\Gamma}{dx} \log re^{i\theta} \cdot dx \\ &= i \frac{1 + \cos \alpha}{4\pi} \frac{d\Gamma}{dx} \log (r \cos \theta + ir \sin \theta) dx \\ &= i \frac{1 + \cos \alpha}{4\pi} \frac{d\Gamma}{dx} \log (x - x' + iz') dx \\ &= i \frac{1 + \cos \alpha}{4\pi} \frac{d\Gamma}{dx} \log (x - x' - iz') dx \\ &= i \frac{1 + \cos \alpha}{4\pi} \frac{d\Gamma}{dx} \log (x - Re^{-i\theta}) dx. \end{aligned}$$

$$\therefore \psi = \text{real part of } \frac{1 + \cos \alpha}{4\pi} \frac{d\Gamma}{dx} \log (x - Re^{-i\theta}) dx.$$

where  $R$  and  $\theta$  are quantities corresponding to  $r$  and  $\theta$  with respect to the  $y$ -axis.

In the case when  $P(x' y' z')$  is very far off from the aeroplane so that  $\cos \alpha = 1$ ,  $\Psi$  ultimately becomes

$$\Psi = \int_{-\frac{b}{2}}^{\frac{b}{2}} \text{real part of } \frac{1}{2\pi} \frac{d\Gamma}{dx} \log (x - Re^{-i\theta}) dx.$$

Integrating by parts,

$$\Psi = \text{real part of } \frac{1}{2\pi} \left[ \Gamma \log(x - Re^{-i\theta}) \right]_{-\frac{b}{2}}^{\frac{b}{2}} \\ - \text{real part of } \frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\Gamma dx}{x - Re^{-i\theta}}$$

since  $\Gamma$  is zero at both the limits

$$\begin{aligned} \Psi &= \text{real part of } \frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\Gamma dx}{-x + Re^{-i\theta}} \\ &= \text{real part of } \frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\Gamma dx}{(x' - x) - iz'} \\ &= \frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\Gamma(x' - x) dx}{x^2 + R^2 - 2xx'} \\ &= -\frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\Gamma \cos \theta}{r} dx. \end{aligned}$$

Similarly

$$\begin{aligned} \Phi &= \frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\Gamma z' dx}{x^2 + R^2 - 2xx'} \\ &= \frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\Gamma \sin \theta}{r} dx. \end{aligned}$$

In this case to find the value of  $u, v, w$  we see that since the vortices are all parallel to the  $y$ -axis,

$$\begin{aligned} u \text{ (due to one vortex filament)} &= -\frac{\partial \Psi}{\partial z} \\ &= -\text{real part of } \frac{\partial}{\partial z} \log(x - Re^{-i\theta}) \frac{d\Gamma}{dx} \frac{dx}{2\pi} \\ &= -\text{real part of } \frac{i}{x - Re^{-i\theta}} \frac{d\Gamma}{dx} \frac{dx}{2\pi} \\ &= -\frac{1}{2\pi} \cdot \frac{z'}{x^2 + R^2 - 2xx'} \frac{d\Gamma}{dx} dx. \end{aligned}$$

$$\begin{aligned}\therefore U = \Sigma u &= -\frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{z'}{x^2 + R^2 - 2xx'} \frac{d\Gamma}{dx} dx \\ &= -\frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{2z'(x-x')\Gamma}{(x^2 + R^2 - 2xx')^2} dx,\end{aligned}$$

since  $\Gamma$  is zero at the limits

$$= -\frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\sin 2\theta}{r^2} \Gamma dx.$$

Similarly,

$$W = \Sigma w = \frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\cos 2\theta}{r^2} \Gamma dx.$$

Hence, when we go far off from the aeroplane but not far off from the vortex sheet we get as the characteristics of the vortex sheet

$$\Phi = \frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\sin \theta}{r} \Gamma dx, \quad \Phi = -\frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\cos \theta}{r} \Gamma dx,$$

$$U = -\frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\sin 2\theta}{r^2} \Gamma dx, \quad W = \frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\cos 2\theta}{r^2} \Gamma dx,$$

and  $r = 0$ ,

where " $r$ " is the distance of the point P from the vortex filament  $\frac{d\Gamma}{dx} dx$ , and  $\theta$  the angle which  $r$  makes with the negative direction of the  $x$ -axis.

We can get the corresponding quantities on the vertical plane through the aeroplane only if we halve these values of  $\phi$ ,  $\psi$ ,  $u$ ,  $v$ ,  $w$ , as the vortex sheet is at a point of the plane only on one side.

### 3.

We have found before that the resistance of an aeroplane to the liquid motion can be completely represented by the amount of energy that is flowing off with the fluid on account of the free vortices going along with it. We can now show that this energy is exactly equivalent to the expression which Prof. Prandtl has found in his "*Tragflügeltheorie*"; thus we shall prove conclusively that it is the energy that is flowing off with the free vortices that constitutes the resistance of the aeroplane.

We have

$$\int q^2 dS = \iint \left\{ \left( \frac{\partial \phi}{\partial x} \right)^2 + \left( \frac{\partial \phi}{\partial z} \right)^2 \right\} dx dz;$$

as we have seen before,  $dS$  is an element of a plane which is parallel to the  $xz$ -plane and very far away from the aeroplane so that we can use the second values of  $\phi, \psi, u, v, w$ , etc.

$$\therefore \int q^2 dS = - \int u \frac{\partial \phi}{\partial x} dx dz - \iint w \frac{\partial \phi}{\partial z} dz dx.$$

Integrating by parts

$$\begin{aligned} &= - \int u \phi dz + \iint \phi \frac{\partial u}{\partial z} dx dz - \int w \phi dx + \iint \phi \frac{\partial w}{\partial z} dz dx \\ &= - \int (lu + nw) \phi ds + \iint \phi \left( \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right) dx dz, \end{aligned}$$

where  $l$  and  $n$  are the direction cosines of the normal of the element of length  $ds$  on the plane; and since the fluid is incompressible and homogeneous

$$\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0.$$

$$\therefore \int q^2 dS = - \int (lu + nw) \phi ds$$

taken over a line enclosing the free vortex sheet; but as there is a discontinuity in the fluid we must take this line-integral over two close lines, one just enclosing the vortex sheet so as to exclude it from the field of consideration and another enclosing the whole system; both these lines are in the plane. If now we extend the latter line so that it becomes an infinitely great circle the value of the integral over it is zero, as when  $R$  is very great  $u$  and  $w$  are of  $1/R^2$  order,  $\phi$  of  $1/R$ , and  $ds$  of  $R$ , so that ultimately we are left with the line just enclosing the vortex sheet only.

Let us take the line as the perimeter of a rectangle just enclosing the sheet so that its length is along the breadth of the sheet and of length  $b$  and its breadth along the thickness of the sheet and of length  $dz$ ; at any point on the length of the rectangle  $l$  is zero and  $n$  is 1 for the upper line and  $-1$  for the lower line; and at any point on the breadth of the rectangle  $n$  is zero and  $u=0$ , so that the values of the integrand are zero at these two short vertical lines. Hence we are left with the value of the integral over the two horizontal parallel lines.

$$\therefore \int q^2 dS = \int (w_1 \phi_1 - w_2 \phi_2) ds,$$

where  $w_1\phi_1$  and  $w_2\phi_2$  are the values of  $w$  and  $\phi$  at the lower line and at a corresponding point on the upper line. But from the above equations for  $\phi, \psi, u, w$  we see that  $w$  is continuous through the vortex sheet, i. e. if we take two corresponding points on opposite sides of the sheet very close to the sheet, then  $w_1 = w_2$ . Hence

$$\int q^2 dS = \int w(\phi_1 - \phi_2) dx;$$

we can now take  $ds$  as equivalent to  $dx$ .

But we find from the above value of  $\phi$  that it is discontinuous, i. e., it has quite opposite values on two corresponding points on opposite sides of the vortex sheet; we have as before

$$\phi = \frac{1}{2\pi} \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\sin \theta}{r} \Gamma dx.$$

We see that  $dx \sin \theta$  is the projection of  $dx$  on a line perpendicular to  $r$ , i. e.  $\frac{dx \sin \theta}{r}$  is the small angle subtended at P by  $dx$ ; if we denote this angle by  $d\alpha$ , then at any point (P) due to the vortex filament at  $x$

$$\phi = \frac{1}{2\pi} \Gamma d\alpha.$$

If now we take P just below the filament on the rectangle, and then just above the filament on the rectangle, then the difference of the angle  $d\alpha$  at the two points is  $2\pi$ ,

$$\text{i. e., } \phi_1 - \phi_2 = \Gamma.$$

Therefore the energy flowing off with the liquid as free vortices is

$$\begin{aligned} \frac{1}{2} \rho \int q^2 dS &= \frac{1}{2} \rho \int_{-\frac{b}{2}}^{\frac{b}{2}} \Gamma w dx \\ &= \frac{1}{4\pi} \rho \int \int_{-\frac{b}{2}}^{\frac{b}{2}} \frac{\cos 2\theta}{r^2} \Gamma_1 \Gamma_2 dx_1 dx_2. \end{aligned}$$

This is exactly the expression found by Prof. Prandtl in the second part of his communication "Tragflügeltheorie." The above expression can never become indeterminate as  $r$  is the distance of a point  $(x_1, 0)$  on the vortex at  $x_1$ , from a point  $(x_2, z_2)$  on the line which is parallel to the  $x$ -axis but at a distance  $z_2$  below in the same vertical plane so that it is just outside the vortex sheet; so that  $r^2 = (x_1 - x_2)^2 + z_2^2$  and can never become zero however small  $z_2$  may be.

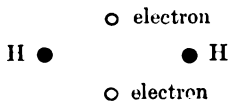


XIII. *Atomic Dimensions and Gaseous Hydride Formation.*

By H. L. RILEY, B.Sc., D.I.C., *Beit Scientific Research Fellow, Demonstrator in Chemistry at the Imperial College of Science and Technology* \*.

THE tendency of two elements to react chemically is dependent on several factors, the chief of which are the orientation of the electrons and the relative dimensions of the atoms or molecules concerned in the reaction. The formation of a gaseous hydride is probably the simplest form of chemical reaction, especially when one considers the formation of the hydride of a gaseous element of low atomic weight. The study of such reactions is most likely to give us some insight into the mechanism of chemical reactivity. The following is an attempt to connect the tendency to hydride formation with atomic dimensions.

According to modern theory, the molecule of hydrogen consists of two positively-charged nuclei and two electrons, arranged probably as follows:—



The two electrons are thought to revolve in some orbit between the two nuclei. Such an arrangement suggests that the molecule of hydrogen will act as a sphere, or as something approximating to a sphere. Hence it is possible, from the known volume of the molecule, to obtain an approximate value of its diameter. This works out to be  $2.5 \times 10^{-8}$ . (Calculated from the mean value of the volume given by the “*b*” in van der Waal’s equation, the viscosity, the thermal conductivity, and the mean free path.)

If one assumes that this value is an approximate measure of the diameter of the electron orbit in the hydrogen molecule, and compares it with the atomic diameters of those elements which form gaseous hydrides, the following interesting fact becomes evident. All those elements which have an atomic diameter less than  $2.5 \times 10^{-8}$  form hydrides with the evolution of energy; and those with an atomic diameter greater than the above value form hydrides with the absorption of energy. The atomic diameters—i. e., the diameter of the outer shell of electrons—of those elements which form gaseous hydrides, together with the heats of formation of their respective hydrides, are appended.

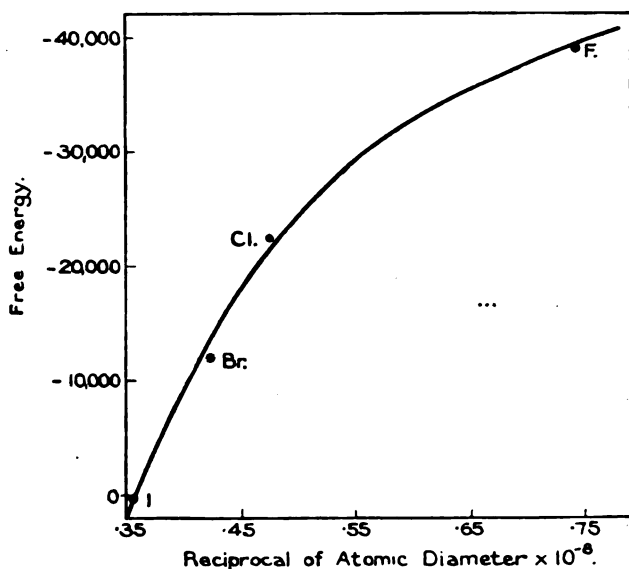
It is not to be expected that there will be any simple quantitative relationship between the atomic diameter and

\* Communicated by Prof. H. B. Baker, C.B.E., M.A., D.Sc., F.R.S.

the heat of formation of the hydride, as the latter is dependent on such factors as temperature and molecular aggregation, being only an approximate measure of the tendency to chemical reaction.

The above seems to indicate that the tendency of an element to form a gaseous hydride is dependent chiefly on the diameter of the atom. If this is less than the diameter of the electron orbit in the hydrogen molecule, then this tendency will be great, because the reacting atom is of such a size that it can easily pierce the orbit and in so doing upset the stability of the electron arrangement in the reacting molecules. The reverse will, of course, be the case when the diameter of the reacting atom is greater than the diameter of the electron orbit in the hydrogen molecule.

Fig. 1.



It may also be pointed out that all elements with an atomic diameter of greater than  $2.5 \times 10^{-8}$  either absorb energy during formation of the hydride or do not react with hydrogen to form a gaseous hydride.

That there probably is some simple relationship between atomic dimensions and the tendency to gaseous hydride formation can be seen in the case of fluorine, chlorine, bromine, and iodine by plotting the reciprocal of the atomic diameter of the halogen against the free energy of the halogen acid.

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It is also interesting to compare the heats of formation of methane, ammonia, water, and hydrofluoric acid.

Hydride .....	$\text{C}\frac{1}{2}\text{H}_2$	$\text{N}\frac{1}{2}\text{H}_2$	$\text{H}\text{O}\frac{1}{2}$	$\text{H}\text{F}$
Heat of formation .....	5.4	4.0	29.0	38.6
Atomic diameter $\times 10^8$	1.54	1.59	1.49	1.35

It will be seen that the heats of formation are in the same order as the reciprocals of the atomic diameters, and this in spite of the fact that the heat of formation of methane is from solid amorphous carbon.

If the above is coincidence, being the relationship between two factors, heat of formation and atomic diameter, both periodic functions of the atomic number, then it is exceedingly difficult to picture the mechanism of a chemical reaction of the above type. The hydrogen molecule is an extremely stable structure, dissociation only occurring partially at the highest attainable temperatures. That another atom is capable of upsetting such a stable arrangement can only be understood when one pictures the atom actually entering the molecule of hydrogen, when electron rearrangement takes place. Energy will be evolved, if the energy liberated by the electron rearrangement is greater than that required to increase the diameter of the electron orbit in the hydrogen molecule, to permit the entry of the reacting atom.

Element.	At. Diam. $\times 10^8$ *	Heat of Formation.
Carbon .....	1.54	$\text{C}_{(\text{amorph.})} + 2\text{H}_2 = \text{CH}_4, +21.7$
Nitrogen .....	1.59	$\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 = \text{NH}_3, +12.0$
Oxygen .....	1.49	$\frac{1}{2}\text{O}_2 + \text{H}_2 = \text{H}_2\text{O}, +58.1$
Fluorine .....	1.35	$\frac{1}{2}\text{F}_2 + \frac{1}{2}\text{H}_2 = \text{HF}, +38.6$
Silicon .....	2.35	$\text{Si}_{(\text{amorph.})} + 2\text{H}_2 = \text{SiH}_4, +8.7$
Phosphorus .....	2.0	$\text{P}_{(\text{white})} + \frac{3}{2}\text{H}_2 = \text{PH}_3, +4.9$
Sulphur.....	2.05	$\text{S}_{(\text{rhombic})} + \text{H}_2 = \text{H}_2\text{S}, +2.7$
Chlorine .....	2.10	$\frac{1}{2}\text{Cl}_2 + \frac{1}{2}\text{H}_2 = \text{HCl}, +22.0$
Arsenic .....	2.52	$\text{As}_{(\text{cryst.})} + \frac{3}{2}\text{H}_2 = \text{AsH}_3, -44.2$
Selenium .....	2.35	$\text{Se}_{(\text{amorph.})} + \text{H}_2 = \text{SeH}_2, +6.0$
Bromine .....	2.38	$\frac{1}{2}\text{Br}_2 + \frac{1}{2}\text{H}_2 = \text{HBr}, +8.4$
Antimony .....	2.80	$\text{Sb}_{(\text{metal})} + \frac{3}{2}\text{H}_2 = \text{SbH}_3, -8.7$
Tellurium .....	2.65	$\text{Te}_{(\text{metal})} + \text{H}_2 = \text{H}_2\text{Te}, -34.9$
Iodine ... ..	2.80	$\frac{1}{2}\text{I}_2 + \frac{1}{2}\text{H}_2 = \text{HI}, -6.1$
Bismuth .....	2.96	.....

\* Prof. W. L. Bragg, *Phil. Mag.* (6) xl. p. 169 (1920).

XIV. *Coupled Cord Pendulums.*  
By CHARLES H. LEES, D.Sc., F.R.S.\*

1. **T**HE interest which has been aroused by oscillograph investigations of the electrical oscillations in the coupled circuits used in wireless telegraphy has led to a revival of the study of coupled dynamical systems in general, and new systems have been invented and their properties studied, either theoretically or experimentally, in order to facilitate the subsequent study of the properties of coupled electrical circuits †.

These studies have added much to our knowledge of the consequences of dynamical coupling, but the results of the theoretical work are not always given in a form which admits of the principal features of the oscillations being readily recognized, nor is it in general easy to see why the experimental curves reproduced have their particular forms under the conditions stated.

The following pages attempt to present the theory of one of the simplest forms of coupled pendulums—that used by Barton and Browning in most of their work,—and to show that by neglecting the small damping which occurs, by using a symmetrical notation and dealing in the fundamental portion of the theory with inclinations rather than with displacements, the work may be reduced to the determination of a certain length which enters into the expression of the periods and amplitudes of the component oscillations which make up the complete oscillation of each pendulum, and that the solution of the problem, so far as it is independent of the initial conditions of the oscillations, can be obtained graphically.

2. Let two simple pendulums (fig. 1) of lengths  $h_1 h_2$  where  $h_2 > h_1$  be suspended from two points  $S_1 S_2$  in the same horizontal plane, and let two points  $B_1 B_2$  on the two pendulums in a horizontal plane  $h$  below the plane of support be joined by an inextensible rod of length equal to  $S_1 S_2$  and of mass negligible in comparison with  $m_1$  and  $m_2$ , the masses of the bobs of the pendulums. Let the oscillations take place in the vertical plane through  $S_1 S_2$ , then the figure  $S_1 S_2 B_2 B_1$  remains a parallelogram throughout the motion.

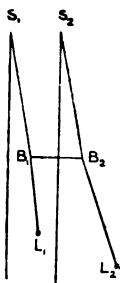
\* Communicated by the Author.

† See e.g. Lyle, *Phil. Mag.* xxv. p. 567 (1913); Barton & Browning, *Phil. Mag.* xxxiv. p. 246 (1917), xxxv. p. 62 (1918), xxxvi. p. 36 (1918); Plummer, *Phil. Mag.* xxxiv. p. 510 (1917); Jackson, *Phil. Mag.* xxxix. p. 284 and xl. p. 329 (1920); Narayan, *Phil. Mag.* xliii. p. 567 (1922).

Let  $\theta, \theta_1, \theta_2$  be the small inclinations to the vertical of the common portion of each pendulum and the independent portions respectively at any time, then the displacements  $x_1, x_2$  of the bobs of the pendulums are

$$\text{and} \quad \left. \begin{aligned} x_1 &= h\theta + (h_1 - h)\theta_1 \\ x_2 &= h\theta + (h_2 - h)\theta_2 \end{aligned} \right\} \dots \dots \dots (2.1)$$

Fig. 1.



The coupled pendulums  $h_1 = S_1L_1 = 13$ ,  $h_2 = S_2L_2 = 15$ ,  
 $h = S_1B_1 = S_2B_2 = 8$ , mass of  $L_1$  : mass of  $L_2 = 3 : 5$ .

For equilibrium at the points B we must have, since the inclinations to the vertical are small,

$$\frac{m_1 + m_2}{\theta_2 - \theta_1} = \frac{m_1}{\theta_2 - \theta} = \frac{m_2}{\theta - \theta_1}.$$

Hence

$$\theta = \frac{m_1}{m_1 + m_2} \theta_1 + \frac{m_2}{m_1 + m_2} \theta_2$$

and

$$\left. \begin{aligned} x_1 &= (h_1 - b_2)\theta_1 + b_2\theta_2 \\ x_2 &= (h_2 - b_1)\theta_2 + b_1\theta_1 \end{aligned} \right\} \dots \dots \dots (2.2)$$

where  $b_1 = \frac{m_1}{m_1 + m_2} h$  and  $b_2 = \frac{m_2}{m_1 + m_2} h$ , may each be looked on as the fraction of  $h$  the common length, prevented by each pendulum from being directly effective as a portion of the length of the other pendulum

Hence

$$\text{and } \left. \begin{aligned} \ddot{x}_1 &= (h_1 - b_2)\ddot{\theta}_1 + b_2\ddot{\theta}_2 \\ \ddot{x}_2 &= (h_2 - b_1)\ddot{\theta}_2 + b_1\ddot{\theta}_1, \end{aligned} \right\} \dots \dots \dots (2.3)$$

where  $\ddot{x}$  signifies differentiation of  $x$  twice with respect to  $t$ .

The equations of motion of the centres of oscillation of the two pendulums are respectively

$$\text{and } \left. \begin{aligned} m_1\ddot{x}_1 &= -m_1g\theta_1 \\ m_2\ddot{x}_2 &= -m_2g\theta_2, \end{aligned} \right\} \dots \dots \dots (2.4)$$

which become on substitution for  $\ddot{x}_1$  and  $\ddot{x}_2$

$$\text{and } \left. \begin{aligned} (h_1 - b_2)\ddot{\theta}_1 + b_2\ddot{\theta}_2 + g\theta_1 &= 0 \\ (h_2 - b_1)\ddot{\theta}_2 + b_1\ddot{\theta}_1 + g\theta_2 &= 0. \end{aligned} \right\} \dots \dots \dots (2.5)$$

On comparing these equations with those we should get for the two pendulums when not coupled, we see that the coefficient of  $\ddot{\theta}_1$  for the first pendulum has been reduced by the coupling from  $h_1$  to  $h_1 - b_2$  and the decrease  $b_2$  made the coefficient of a term in  $\ddot{\theta}_2$ , while for the second pendulum the coefficient of  $\ddot{\theta}_2$  has been reduced from  $h_2$  to  $h_2 - b_1$  and the decrease  $b_1$  made the coefficient of a term in  $\ddot{\theta}_1$ . As these reduced lengths appear frequently in the subsequent equations, we shall write  $l_1$  for  $h_1 - b_2$  and  $l_2$  for  $h_2 - b_1$ , so that the equations become

$$\text{and } \left. \begin{aligned} l_1\ddot{\theta}_1 + b_2\ddot{\theta}_2 + g\theta_1 &= 0 \\ l_2\ddot{\theta}_2 + b_1\ddot{\theta}_1 + g\theta_2 &= 0 \end{aligned} \right\} \dots \dots \dots (2.5')$$

For convenience we shall suppose that  $l_2 > l_1$ .

Multiplying the second equation by  $\lambda/b_1$ , where  $\lambda$  is a quantity to be determined, and subtracting from the first, we get

$$(l_1 - \lambda)\ddot{\theta}_1 + \left(b_2 - \frac{\lambda l_2}{b_1}\right)\ddot{\theta}_2 + g\left(\theta_1 - \frac{\lambda}{b_1}\theta_2\right) = 0, \quad (2.6)$$

which may be integrated directly if

$$\frac{b_2 - l_2\lambda/b_1}{l_1 - \lambda} = -\frac{\lambda}{b_1};$$

that is if

$$\lambda_2 + (l_2 - l_1)\lambda - b_1b_2 = 0,$$

which gives

$$\left. \begin{aligned} \lambda \\ \lambda' \end{aligned} \right\} = -\frac{l_2 - l_1}{2} \pm \sqrt{\left(\frac{l_2 - l_1}{2}\right)^2 + b_1b_2}. \quad (2.7)$$

K 2

The integrals of the equations are then

$$\begin{aligned} \theta_1 - \frac{\lambda}{b_1} \theta_2 &= f \sin \left( \sqrt{\frac{g}{l_1 - \lambda}} \cdot t + \phi \right) \\ \text{and} \quad \theta_1 - \frac{\lambda'}{b_1} \theta_2 &= s \sin \left( \sqrt{\frac{g}{l_1 - \lambda'}} \cdot t + \sigma \right), \end{aligned} \quad (2.8)$$

where  $f, \phi$  for the faster oscillation and  $s, \sigma$  for the slower are constants of integration.

Solving for  $\theta_1$  and  $\theta_2$ , substituting  $-\frac{b_1 b_2}{\lambda}$  for  $\lambda'$  in the amplitude terms and  $l_2 + \lambda$  for  $l_1 - \lambda'$  in the circular functions so as to retain only that root of the equation in  $\lambda$  which vanishes when the pendulums are not coupled, and writing

F for  $\frac{b_1 b_2}{b_1 b_2 + \lambda^2} f$ , S for  $\frac{b_1 \lambda}{b_1 b_2 + \lambda^2} s$ , we get

$$\begin{aligned} \theta_1 &= \left. \begin{aligned} &F \sin \left( \sqrt{\frac{g}{l_1 - \lambda}} \cdot t + \phi \right) \\ &+ \frac{\lambda}{b_1} S \sin \left( \sqrt{\frac{g}{l_2 + \lambda}} \cdot t + \sigma \right) \end{aligned} \right\} \\ \text{and } \theta_2 &= -\frac{\lambda}{b_2} \left. \begin{aligned} &F \sin \left( \sqrt{\frac{g}{l_1 - \lambda}} \cdot t + \phi \right) \\ &+ S \sin \left( \sqrt{\frac{g}{l_2 + \lambda}} \cdot t + \sigma \right) \end{aligned} \right\}. \end{aligned} \quad (2.9)$$

Thus the four quantities F, S,  $\phi$ ,  $\sigma$  remain to be determined by the initial conditions of the system.

On substituting for  $\theta_1$  and  $\theta_2$  in the equations (2.2) for  $x_1$  and  $x_2$ , we find on reduction

$$\begin{aligned} x_1 &= \left. \begin{aligned} &F' \sin \left( \sqrt{\frac{g}{l_1 - \lambda}} \cdot t + \phi \right) \\ &+ \frac{\lambda}{b_1} S' \sin \left( \sqrt{\frac{g}{l_2 + \lambda}} \cdot t + \sigma \right) \end{aligned} \right\} \\ \text{and } x_2 &= -\frac{\lambda}{b_2} \left. \begin{aligned} &F' \sin \left( \sqrt{\frac{g}{l_1 - \lambda}} \cdot t + \phi \right) \\ &+ S' \sin \left( \sqrt{\frac{g}{l_2 + \lambda}} \cdot t + \sigma \right) \end{aligned} \right\}. \end{aligned} \quad (2.9')$$

where  $F' = (l_1 - \lambda)F$ ,  $S' = (l_2 + \lambda)S$ ,  $\phi$ ,  $\sigma$  are again constants.

3. On comparing these expressions with those which would hold if the pendulums were not coupled,

$$\left. \begin{aligned} x_1 &= F' \sin \left( \sqrt{\frac{g}{h_1}} \cdot t + \phi \right) \\ x_2 &= S' \sin \left( \sqrt{\frac{g}{h_2}} \cdot t + \sigma \right), \end{aligned} \right\}$$

we note that the effect of the coupling is to replace  $h_1$  by  $l_1 - \lambda$  in the case of the faster and  $h_2$  by  $l_2 + \lambda$  in the case of the slower pendulum, and that each of these new oscillations is reproduced in the oscillation of the pendulum from which it is not directly derived, with an amplitude reduced in the ratio  $\lambda/b_1$  in the case of the slower and  $-\lambda/b_2$  in that of the faster oscillation.

With the help of this observation it is possible to write down the equations 2.9 or 2.9' directly from inspection of fig. 1.

It will be noticed that as the signs of the amplitudes  $\frac{\lambda}{b_1} S$  and  $S$  or  $\frac{\lambda}{b_1} S'$  and  $S'$  of the slower component oscillations of each pendulum are the same, the slower component oscillations are in phase. As those of the amplitudes  $F$  and  $-\frac{\lambda}{b_2} F$  or  $F'$  and  $-\frac{\lambda}{b_2} F'$  of the faster component oscillations are different, the faster component oscillations are opposite in phase.

The product of the amplitudes of the component oscillations of the first pendulum is  $FS\lambda/b_1$ , while that for the second is  $-FS\lambda/b_2$ . The quotient of the first product by the second is  $-b_2/b_1$ , that is  $-m_2/m_1$  \*.

The ratios of the products of the maximum angular or linear velocities and of the products of the maximum angular or linear accelerations of the component oscillations of the two pendulums have also the same value,  $-m_2/m_1$ .

The kinetic energy  $T$  of the system is  $\frac{1}{2}m_1\dot{x}_1^2 + \frac{1}{2}m_2\dot{x}_2^2$ . On substituting the values of  $x_1$  and  $x_2$  from the equations 2.9' and reducing, we get

$$T = \frac{1}{2}g \left( 1 + \frac{\lambda^2}{b_1 b_2} \right) \left\{ m_1 (l_1 - \lambda) F^2 \cos^2 \left( \sqrt{\frac{g}{l_1 - \lambda}} \cdot t + \phi \right) + m_2 (l_2 + \lambda) S^2 \cos^2 \left( \sqrt{\frac{g}{l_2 + \lambda}} \cdot t + \sigma \right) \right\}. \quad (3.1)$$

\* See Rowell, Phil. Mag. xliv. p. 382 (1922).



The potential energy  $V$  of the system is

$$\begin{aligned} & \frac{1}{2}m_1g\{h\theta^2 + (l_1-h)\theta_1^2\} + \frac{1}{2}m_2g\{h\theta^2 + (h_2-h)\theta_2^2\}, \\ \text{which reduces in virtue of equations (2.2) and (2.9) to} \\ V = & \frac{1}{2}g\left(1 + \frac{\lambda^2}{b_1b_2}\right)\left\{m_1(l_1-\lambda)F^2\sin\left(\sqrt{\frac{g}{l_1-\lambda}}\cdot t + \phi\right)\right. \\ & \left.+ m_2(l_2+\lambda)S^2\sin\left(\sqrt{\frac{g}{l_2+\lambda}}\cdot t + \sigma\right)\right\}. \quad (3.2) \end{aligned}$$

Hence the sum of the energies

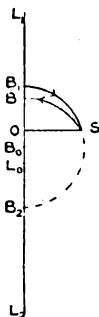
$$T + V = \frac{1}{2}g\left(1 + \frac{\lambda^2}{b_1b_2}\right)\{m_1(l_1-\lambda)F^2 + m_2(l_2+\lambda)S^2\}, \quad (3.3)$$

which is constant.

4. Before discussing special cases of the general result (2.9), it is convenient to give it a geometrical form.

In a vertical straight line (fig. 2) let  $B_1B_2$  be taken equal

Fig. 2.



$B_1B_2 = h$ ,  $B_1L_1 = h_1 - h$ ,  $B_2L_2 = h_2 - h$ ,  $(OB_1 = b_1) : (OB_2 = b_2) = m_1 : m_2$ .

$B_1S$  arc with  $B_0$  the middle of  $B_1B_2$  as centre,  $SB$  arc with  $L_0$  the middle of  $L_1L_2$  as centre,  $OB = \lambda$ . Component oscillations are those of  $BL_1$  and  $BL_2$ . Amplitude ratios of first pendulum to second =  $-OB_2/OB$  for faster =  $OB/OB_1$  for slower components.

on some convenient scale to the length of the common portion  $h$  of each pendulum. Let  $B_2L_2$  be the free length of one (*e.g.* the longer) and  $B_1L_1$  that of the other pendulum. Let  $O$  divide  $B_1B_2$  in the ratio  $m_1 : m_2$  so that

$$B_1O = \frac{m_1}{m_1 + m_2} B_1B_2 = \frac{m_1}{m_1 + m_2} h$$

and

$$OB_2 = \frac{m_2}{m_1 + m_2} B_1B_2 = \frac{m_2}{m_1 + m_2} h.$$

Through O draw the horizontal OS. With  $B_0$ , the middle point of  $B_1B_2$  as centre, describe a circular arc cutting the horizontal through O in S. Then  $OS = \sqrt{b_1b_2}$ . With  $L_0$  the middle point of  $L_1L_2$  as centre, describe a circular arc SB cutting  $OB_1$  in B. Then, since  $OL_1 = l_1$  and  $OL_2 = l_2$ ,

$$OL_0 = \frac{l_2 - l_1}{2} \text{ and } BL_0 = L_0S = \sqrt{\left(\frac{l_2 - l_1}{2}\right)^2 + b_1b_2}.$$

Thus

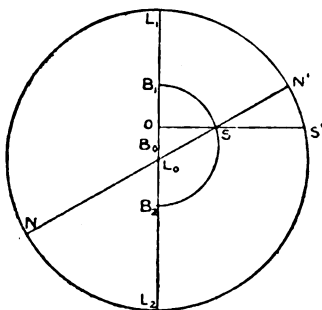
$$OB = \sqrt{\left(\frac{l_2 - l_1}{2}\right)^2 + b_1b_2} - \frac{l_2 - l_1}{2} = \lambda,$$

$BL_1 = l_1 - \lambda$  and  $BL_2 = l_2 + \lambda$ , so that  $BL_1$  and  $BL_2$  are the lengths of the simple pendulums which have times of oscillation equal to those of the faster and slower component oscillations from which the actual oscillations of the two pendulums are compounded.

The ratio of the amplitude of the faster component oscillation of the first pendulum to that of the second is  $-b_2/\lambda$ , that is  $-OB_2/OB$ ; while the ratio of the amplitude of the slower component of the first to that of the second is  $\lambda/b_1$ , that is  $OB/OB_1$ . The product of the ratios is  $-m_2/m_1$ .

The geometrical construction of fig. 2 thus gives all the quantities which result from the analysis of section 2.

Fig. 3.



Component oscillations those of N'S and SN. Coupling  $\gamma = \frac{OS}{OS'}$ .

When the periods of the component oscillations only are required, it is simpler after finding S to join it to  $L_0$  and produce to cut the circle on  $L_1L_2$  as diameter in N and N' (fig. 3). Then SN and SN' are the lengths of the simple pendulums which give the component oscillations.

If, in fig. 3, OS be produced to cut the circle on  $L_1L_2$  as diameter in S', the ratio  $OS/OS' = \sqrt{b_1b_2/l_1l_2}$  is what Barton

and Browning propose \*, in analogy with the terminology in use in connexion with coupled electric circuits, to call the "coupling  $\gamma$ " of the two pendulums.

As the length  $\lambda$  plays so important a part in the determination of the oscillations of the system, it would be useful to give it a name—*e.g.*, the "linking" or "key" length.

### 5. Consideration of special cases.

*Case 1.*—The lengths of the pendulums are equal and their masses equal. This is the simplest case. For it,  $O$ ,  $B_0$ , and  $L_0$  all coincide and  $B$  coincides with  $B_1$ . Thus the periods of the component oscillations are those of pendulums of lengths  $B_1L_1$  and  $B_1L_2$ , that is  $h_1-h$  and  $h_2$ , and the ratio of the amplitudes of the component oscillations of the first pendulum to that of the second are  $-B_0B_2/B_0B_1 = -1$  for the faster and  $B_0B_1/B_0B_1 = 1$  for the slower. The values of  $F$  and  $S$ ,  $\phi$  and  $\sigma$  depend on the initial conditions of the motion. If these conditions are such that  $F=S$ , each pendulum in turn comes to rest when the other has its oscillation† of maximum amplitude.

*Case 2.*—The lengths of the pendulums unequal, but their masses equal. In this case  $O$  and  $B_0$  of fig. 2 coincide, but  $B$  is not identical with  $B_1$ . The amplitude ratios of the first pendulum to the second are for the faster component oscillation  $-B_0B_2/B_0B$  and for the slower  $B_0B/B_0B_1$  which are numerically reciprocals. If the initial conditions are such as to make the amplitudes of the faster and slower component oscillations of one pendulum equal, that pendulum comes to rest while the other has its oscillation of maximum amplitude; but we no longer have each pendulum in turn coming to rest while the other has its oscillation of maximum amplitude‡.

*Case 3.*—With the masses  $m_1$  and  $m_2$  unequal but the lengths  $h_1$  and  $h_2$  equal we have  $l_1$  and  $l_2$  unequal, and in fig. 2  $B_0$  and  $L_0$  coincide; the two circles are concentric, and therefore  $B$  and  $B_1$  coincide. Thus the amplitude ratio of the first to the second pendulum is for the faster component oscillation  $-OB_2/OB_1$  and for the slower component oscillation  $OB_1/OB_1 = 1$ . The initial conditions might be such as to make the two component oscillations of one pendulum equal in amplitude, but those of the other would then be unequal.

\* Phil. Mag. xxxiv. p. 254 (1917).

† See Barton & Browning, Phil. Mag. xxxiv. p. 255 (1917) and the curves given by them for this case.

‡ Barton & Browning, Phil. Mag. xxxv. p. 71 (1918), equations (69) and (70) and the curves 20-28 illustrating such cases.

It would be possible to have one pendulum coming to rest when the amplitude of the oscillation of the other was a maximum, but the other would not come to rest\*.

*Case 4.*—In the general case in which neither the masses  $m_1$  and  $m_2$  nor the lengths  $h_1$  and  $h_2$  are equal,  $l_1$  and  $l_2$  are unequal, and in fig. 2  $O$ ,  $B_0$ , and  $I_0$  are distinct points.  $B$  does not coincide with  $B_1$ , the amplitude ratios are unequal, and it would again be possible by adjusting the initial conditions to secure that one only of the pendulums should have the same amplitude for each of its component oscillations. Hence only one of the two pendulums could have zero amplitude at the time that the other had its oscillation of maximum amplitude†.

It is possible that with inequality of the masses  $m_1$  and  $m_2$  and inequality of the lengths  $h_1$  and  $h_2$  we may have  $l_1 = l_2$ . In that case  $O$  and  $I_0$  of fig. 2 coincide, but  $B_0$  does not coincide with either, nor does  $B$  with  $B_1$ . Thus the amplitude conditions are those of the general case.

6. The effect of changing the value of one of the variables  $m_1$ ,  $m_2$ ,  $h_1$ ,  $h_2$ , and  $h$  may be traced readily by reference to fig. 2. Thus when  $m_1$  is very small compared with  $m_2$ ,  $OB_1$  is small compared with  $OB_2$ ,  $OS$  is small, and  $B$  close to  $B_1$  and between  $B_1$  and  $O$  if  $l_2$  is greater than  $l_1$ . The faster component oscillations correspond to those of a pendulum of length slightly greater than  $h_1 - h$  the free length of the shorter pendulum, and the slower oscillations to those of a pendulum of length slightly less than  $h_2$  the total length of the longer pendulum.

As the mass  $m_1$  increases in proportion to  $m_2$ ,  $OB_1$  increases at the expense of  $OB_2$ ,  $OS$  increases, and  $B$  separates more from  $B_1$ . The faster component oscillation therefore slows down and the slower speeds up, and when the two masses are equal, the faster oscillation is that of a pendulum of length

$$\frac{h_1 + h_2 - h}{2} - \sqrt{\left(\frac{h_2 - h_1}{2}\right)^2 + \left(\frac{h}{2}\right)^2},$$

and the slower that of one of length

$$\frac{h_1 + h_2 - h}{2} + \sqrt{\left(\frac{h_2 - h_1}{2}\right)^2 + \left(\frac{h}{2}\right)^2}.$$

\* Compare Barton & Browning, Phil. Mag. xxxv. p. 66 (1918), equations (27) and (28) (which, however, include damping) and the curves 1-19 illustrating these cases.

† Compare Barton and Browning, Phil. Mag. xxxvi. p. 40 (1918), equations (21) and (22) (which, however, include damping) and the curves in illustration.

If  $m_1$  increases still further,  $OB$  becomes greater than  $OB_2$ , and the slowing down of the faster and the speeding up of the slower component oscillations continues. When  $O$  coincides with  $L_0$ ,  $l_1 = l_2$ .

It will be noticed that the amplitude ratios are not affected by a change in the distances  $B_1L_1$ ,  $B_2L_2$  of fig. 2 so long as  $L_0$ , the middle point of  $L_1L_2$ , remains fixed. Hence the lengths of the independent portions of the pendulums may be increased or decreased each by the same amount without change of the amplitude ratios given by  $OB$ ,  $OB_1$ , and  $OB_2$ . In particular,  $B_1L_1$  may be made zero, and fig. 2 then gives the solution of the problem of the oscillations of a system consisting of one simple pendulum suspended from the bob of another simple pendulum.

7. From the preceding paragraphs it will have been seen that the whole of the dynamics of coupled pendulums of the type here considered may be represented by the graphical construction of fig. 2, which entails the drawing of two straight lines and two arcs of circles. It determines the periods of the faster and slower component oscillations, the ratio of the amplitudes of the faster components and the ratio of the amplitudes of the slower components. To complete the solution of any particular case, we require in addition the actual values of the amplitudes and one of the faster and one of the slower component oscillations and the two phase angles. This further information may be furnished by the initial conditions or by the conditions at some other time or times.

In all cases in which the periods of the component oscillations are commensurate, it is possible to find an instant  $t_0$  from which to reckon the time, which will rid our equations of the phase angles. Thus, if  $t_0$  satisfies the equations

$$\sin\left(\sqrt{\frac{g}{l_1 - \lambda}} \cdot t_0 + \phi\right) = \sin\left(\sqrt{\frac{g}{l_2 + \lambda}} \cdot t_0 + \sigma\right) = 0, \quad (7.1)$$

that is

$$t_0 = \frac{n\pi - \phi}{\sqrt{\frac{g}{l_1 - \lambda}}} = \frac{n'\pi - \sigma}{\sqrt{\frac{g}{l_2 + \lambda}}},$$

where  $n$  and  $n'$  are suitable integers, and we reckon time  $t$  from the instant  $t_0$ , the equations for the angular oscillations

of the pendulums take the form

$$\left. \begin{aligned} \theta_1 &= F \sin \sqrt{\frac{g}{l_1 - \lambda}} \cdot t + \frac{\lambda}{b_1} S \sin \sqrt{\frac{g}{l_2 + \lambda}} \cdot t, \\ \theta_2 &= -\frac{\lambda}{b_2} F \sin \sqrt{\frac{g}{l_1 - \lambda}} \cdot t + S \sin \sqrt{\frac{g}{l_2 + \lambda}} \cdot t, \end{aligned} \right\} \quad (7.2)$$

with corresponding equations for the linear displacements of the bobs of the two pendulums.

In either case it is usual to represent the compound oscillation of each pendulum by means of a curve with time as abscissa and the angular or linear displacement as ordinates. The shape of each of these curves is generally of greater interest than the absolute values of the ordinates, so that the ratio of the amplitude of the faster to that of the slower component oscillation of each pendulum is sufficient for most purposes. This ratio may have values ranging from  $-\infty$  to  $+\infty$  in different cases, but it is convenient in drawing the curves to take each as having the same maximum ordinate, say 1, that is the sum of the amplitudes of the quicker and slower component oscillations in each case = 1, and therefore each of the amplitudes may vary in magnitude between 0 and 1. The gradual change of shape of the compound oscillation as the ratio of the amplitudes of the two component oscillations changes from 0 to  $\infty$  may be sufficiently illustrated by taking five intermediate stages between the extreme cases in which either component is present alone.

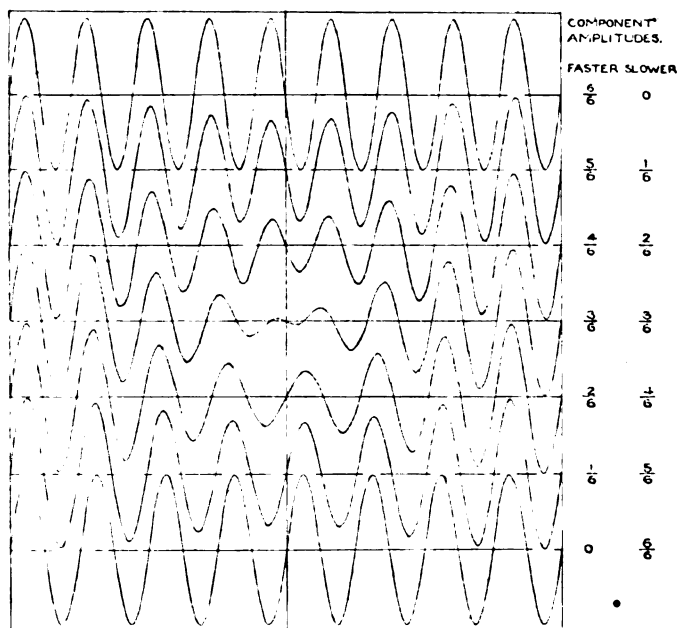
3. The periods of the component oscillations may bear any ratio to each other, but in a great number of the most interesting cases the ratio approximates to that of two consecutive integers exceeding 4 or 5 to each other. The compound oscillations in all these cases show the same principal features, and may be represented by a typical example. In fig. 1 the lengths of the two pendulums are as 13 : 15, their common part 8 and their masses as 3 : 5. A more interesting case is that of two pendulums of lengths  $h_1=40$  and  $h_2=42$  with a common length  $h=8$ , the ratio of the masses 3 : 5, so that fig. 2 still holds (section 6) if  $B_1L_1$  and  $B_2L_2$  are each increased by 27 units. In this case  $b_1=3$ ,  $b_2=5$ ,  $l_1=35$ ,  $l_2=39$ ,  $l_2-l_1=4$ ,  $\lambda=2\cdot36$ ,  $l_1-\lambda=32\cdot64$ ,  $l_2+\lambda=41\cdot36$ , the ratio of the frequencies of the component oscillations is 9/8 and the coupling (sect. 4) 0.104, *i.e.* 10.4 per cent.

The curves of fig. 4 show the results of compounding two oscillations of frequencies in this ratio with amplitudes of

the faster and the slower oscillations respectively 1 and 0, 5/6 and 1/6, 4/6 and 2/6, 3/6 and 3/6, 2/6 and 4/6, 1/6 and 5/6, 0 and 1. In each curve the two component oscillations are in the same phase at the left-hand and right-hand margins, and opposite in phase at the middle line of the diagram.

If we assume that in a particular case the initial conditions are such that for the pendulum  $h_1$  at the epoch from which time is measured, the ratio of the amplitudes of fast to slow component is 5 to 1 and the two components are in phase,

Fig. 4.



Oscillations compounded of two components of frequencies as 9:8, and amplitudes stated.

the second curve from the top of the diagram represents the compound oscillation. But this fixing of the ratio  $F'/b_1 S'$  of the amplitudes of the components for one pendulum also fixes it for the other, for which, according to equation (2.9), it must have the value  $-\frac{\lambda}{b_2} F'S'$ , that is  $-\lambda^2/b_1 b_2$  times the former, or  $-0.371 \times 5 = -1.85$ . The compound oscillation of the second pendulum is therefore represented by a curve nearly identical with the third curve from the top of the diagram.

But since the component oscillations are opposite in phase at the epoch from which time is reckoned, that part of the curve for the second pendulum between the middle line and the right-hand margin of the diagram corresponds to that between the left-hand margin and the middle line in the case of the first pendulum.

Assuming any other ratio for the amplitudes of the component oscillations of one pendulum, we fix in the same way the ratio for the other, and in each case select from the curves of fig. 4 those which represent most nearly the compound oscillation of each pendulum.

For accurate work a set of curves would be necessary for each value of the ratio of the frequencies of the component oscillations; but so long as the ratio is that of two consecutive integers not less than 4, the principal features of the various sets are the same, and fig. 4 illustrates sufficiently the insight the graphical method of fig. 2 is capable of giving into the problems of coupled pendulums in cases where the damping is negligible.

#### XV. *Dimensional Analysis*. By EDGAR BUCKINGHAM\*.

IN an interesting article under this heading in the March number of the *Philosophical Magazine*, Dr. Norman Campbell expresses some dissatisfaction with the manner in which the late Lord Rayleigh's method of reasoning from dimensions has been used, or abused, in recent years. I agree, in substance, with much of what he says, and yet I think the final impression he leaves is false because he exaggerates the unimportance, uselessness, and unreliability of the method. Physicists who have learned from experience the value of dimensional reasoning, the principle of similarity, or whatever else it may be called, will not be much affected by arguments either for or against it. But since, in Dr. Campbell's article passed without comment, those who have not acquired this familiarity might be led to suppose that the subject was not worth cultivating, it seems well to note that some other points than those particularly emphasized by Dr. Campbell also deserve attention.

As regards the question of utility—that is a purely practical matter to be settled by experience. It is much like the question whether it is better to use a slide-rule, a log table,

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or longhand computation : it depends on circumstances and also partly on taste or habit. But that the method has been very useful can be proved beyond a doubt without going outside the limits of London. One has only to examine the reports of the National Physical Laboratory and the brilliant record of experimental work by the Staff of the Engineering and Aerodynamics Departments to be convinced that dimensional analysis—to give it its most convenient name, in despite of Dr. Campbell—has been a very valuable tool. The members of the N. P. L. have not, to be sure, *talked* much about the method : they have been too busy with interesting and difficult experiments to spend time in explaining the details of what seemed to them simple and obvious. But they have *used* it constantly ; and if they have ever been led astray by it, I do not remember their saying so.

The contemplation of the very fine series of investigations just referred to, leads naturally to the question what sort of things dimensional analysis is most useful for ; and in the answer there is, I think, one main reason for the difference between Dr. Campbell's feeling toward the subject and mine.

The dimensional method has often been employed for the purpose of deducing new relations in pure physics without going through more laborious investigations of which it was evident beforehand that the results would involve unknown constants. This is the way in which Lord Rayleigh used the method most, a good example being his  $\lambda^4$  relation for scattered light. I suspect that this is the sort of problem in which Dr. Campbell is most interested, but it is the one in which it is easiest to make mistakes. And if he can catch Jeans or Einstein in a slip, the rest of us may enjoy the joke without any malice, for they can afford to slip occasionally.

But the principal value of dimensional analysis is not for obtaining new theoretical results or for proving anything *a priori*. No new result can be proved, to demonstration, except by experiment ; for theoretical physics, of whatever sort, can only say that *if* so and so is true, and *if* we have not overlooked anything, then something else must also be true. As long as there is an *if* anywhere, the final decision rests with experiment. The main value of dimensional analysis is as a guide in planning experimental work and, particularly, in analysing and interpreting the observational results. The more complicated the problem and the greater the number of variables involved, the more useful does such a guide become ; and this remark leads directly to the consideration of another point in Dr. Campbell's paper.

He deplores the eruption of ill-digested dimensions in the

last few years, and seems to imply that some degree of responsibility for this state of things rests on those who, being convinced of the utility of the dimensional method, have attempted to expound it in an elementary textbook style, so as to induce others to try it. But this reproach, if intended, is wide of the mark; for it is perfectly obvious that the immediate occasion for the recent great increase in the use of dimensional arguments is the complete demonstration of their value by the Staff of the N. P. L., which has led others to take up the method until now it is used everywhere.

There is, however, a more fundamental reason for the increased popularity of the dimensional method. Lord Rayleigh used it in 1871 in one of his earliest papers, he was interested in it all his life, and he employed it freely in numerous cases; and yet no one else had used it much until recently. Why is this? The answer is, clearly, that technical physics, the physics of engineering and manufacturing processes, has had an immense development in the last dozen years, and that it is precisely in technical physics that dimensional analysis is of most value and importance.

In the experimental researches in pure physics, with which most physicists are occupied, it is usually possible so to control conditions that the theory of the experiment shall be simple. The number of variables can be kept small, it is easy to write down the differential equations, and—this is the important point—the experiment can be so arranged that the equations which describe it can be solved without great labour. When this is impossible, the investigator who is free to suit himself is likely to turn to some more tractable problem, for there are still plenty of them.

But in technical physics we find a very different state of affairs. Problems which are clamouring for solution must be taken up as they are, with all their complications, and cannot be thrown aside merely because they are difficult. It is often not possible to isolate each separate phase of the problem, investigate it by itself, and then get the general solution by synthesis. It may be a difficult matter to write down any equation or set of equations for describing the phenomenon in question; and even if equations have been obtained, it is usually obvious that the task of solving them would be impracticably laborious and time-consuming, if not altogether impossible. It is just in such cases that the rough and ready method of dimensions comes in handy and proves itself very much better than nothing at all.

No one, of course, will think of denying that when ordinary methods will work, the definite results to which they lead are

worth more than anything that can be got from dimensional analysis alone; but the question is: "is half a loaf better than no bread?" and not whether it is better than a whole cake. And even here a counter attack may be made. For, as Professor W. F. G. Swann once remarked: it often happens that when, by a long mathematical process, we have obtained some formidable combination of symbols with a numerical coefficient, the correct value of the coefficient remains doubtful and the only part we are sure is right might just as well have been obtained by dimensions. There is truth in this remark along with its exaggeration.

Dr. Campbell's main contentions are, I take it, 1st that we can never be certain that our dimensional treatment of any problem is correct unless we have actually written down the differential equations; 2nd that if we have done this, we can get all the information obtainable from the principle of dimensional homogeneity by mere inspection of the equations, so that all cumbersome algebraic machinery, such as that of the  $\Pi$  theorem, is superfluous; and 3rd that, being both cumbersome and superfluous, it should be buried and forgotten.

To the first of these it may be remarked that we are never absolutely sure of anything in physics till it has been proved by experiment, even if we have written down a differential equation; and that in almost any operation, avoiding mistakes is a matter of care, experience, and skill. A lawyer trying to drive a nail may hit his fingers, whether he uses a hammer or a hatchet: an expert carpenter is less likely to do so, and he will use whichever tool is the more convenient in view of the other things he may be having to do in connexion with driving the nail.

The second point may be granted without discussion,—the carpenter's hammer is not indispensable; but it is a very useful tool even though one cannot chop with it.

The third point may be left for the future to decide. I think that beginners will find the  $\Pi$  theorem a good thing to cut their teeth on: but in any event, after one has reached the stage in which all the results obtainable by the formal algebra are evident upon mere inspection, one need no longer pay any attention to it. I came upon the  $\Pi$  theorem in the course of trying to follow the reasoning in some of the papers in the early volumes of the N. A. C. A. Reports, and found it advantageous to have the theorem stated in some detail; but the form in which the dimensional argument is put is of small importance: what counts is its utility to people who know how to use it, and that is indisputable. In reference to the question how Lord Rayleigh would have felt about the

formal discussion of the dimensional method, I may quote from a letter of October 30, 1915, in which he wrote, regarding my first attempt, in the 'Physical Review' of Oct. 1914: "It is the best exposition of the subject I have come across; the only doubt is whether it is not too good for a majority of Physicists!" And three months later, after some correspondence: "I hope you will continue your work on this subject."

To anticipate all the possible mistakes that might be made in the name of dimensions would require omniscience, but many physicists of quite ordinary endowments have found the method of dimensions so useful that they accept the risk with equanimity. Their salvation lies not in formal logic, not in differential equations, and not in arguments about the dimensions of particular quantities which may always be stated in various ways, but, as Dr. Campbell implies, in physical common sense.

Washington,  
April 8, 1924.

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XVI. *Note on a Search for the missing Element No. 43.*  
By C. H. BOSANQUET and T. C. KEELEY \*.

THE smallest atomic number corresponding to an element not yet detected is 43, an element which from its place in the periodic table should be a metal resembling Manganese in its reactions.

During the past year a number of manganese minerals have been investigated in hopes of detecting this element, as it was considered possible that amounts of the order of 1 per cent. might have escaped detection by chemical methods in such minerals. The results have, so far, been negative.

The method used in the investigation was to photograph the X-ray spectrum of each mineral between the wavelengths 620 and 720 X.U.

*Experimental.*

The tube used had an anti-cathode whose face was horizontal and normal to the cathode-ray stream, and viewed edgewise this constituted a line source of X-rays sufficiently sharp to allow one to dispense with collimator slits.

\* Communicated by Prof. F. A. Lindemann, F.R.S.

*Phil. Mag.* S. 6. Vol. 48. No. 283. July 1924. L

A piece of calcite with a face about 4 cm. long, in the direction of the rays served as grating; it was fixed in position about 25 cm. from the anti-cathode and equidistant from the anti-cathode and the plate-holder, a lead screen with a slit 6 mm. wide placed immediately in front of the crystal serving to protect the plate from direct radiation. The crystal was a very perfect specimen, and gave no trouble through irregularities of the face, so that it was unnecessary to rock it. Adjustment was tested by photographing the K spectrum of molybdenum (42) which just covers the range required, the crystal being large enough to take in the whole spectrum at one setting. The  $K\alpha$  line of 43 would occur approximately midway between the  $K\alpha$  and  $K\beta$  lines of molybdenum. The apparatus gave a dispersion of approximately 10 X.U. per mm., the resolving power being always sufficient to separate the  $K\alpha$  doublet of molybdenum.

The minerals, in some cases mixed with a small quantity of Mo filings, were fused with the oxyhydrogen flame into small nickel cups lined with alundum cement, and then ground down flush with the edges of the cups. The cups were screwed into the removable anti-cathode holder, which located them sufficiently exactly to ensure the  $K\alpha$  line of 43 coming into the field.

The exposures were never less than 1 milliampere hour at 50 k.v., which was sufficient to show the presence of 0.2 per cent. of added Mo, and in several cases, when the tube was running well, the exposures were much longer than this.

In most cases it was necessary to pass a discharge for several hours with the pump working before it was possible to maintain a potential difference of as much as 40 k.v. across the tube, but when the tube had become sufficiently hard to give off Mo rays in considerable quantities, it passed in an hour or so through several stages of increasing hardness. In the final stages it was possible to shut off the pump completely, and eventually air had to be admitted at frequent intervals in order to keep the tube sufficiently soft. This was very conveniently accomplished by using a good tap with a long lever fixed to it to allow of fine adjustment; the tap communicated directly with the atmosphere.

The current which could be used varied, according to the mineral used and the state of the tube, between 1 and 0.2 m.a., the anti-cathode being maintained at a fairly bright red heat.

*Minerals used.*

The origin of the minerals used is given in the second column; in a few cases no information was available on this point.

<i>Mineral.</i>	<i>Origin.</i>
Psilomelane.	Broken Hill, Australia.
Psilomelane.	Bohemia.
Rhodonite.	Perm, Russia.
Rhodonite.	Chikhla, Central Prov., India.
Rhodochrosite.	Hungary.
Rhodochrosite.	Park Co., Col., U.S.A.
Polyanite.	Upton Pike (Exeter?).
Pyrolusite.	Davidson's Mine, King's Co.
Pyrolusite.	Newton Down (Devon?).
Wad.	Bohemia.
Manganite.	UNKNOWN ORIGIN.
Franklinite.	
Pyrolusite.	
Psilomelane.	

In addition to these minerals there were also examined a specimen of Mn extracted from Torbernite supplied by Dr. A. S. Russell, the mixed Ni, Co, and Mn extracted from Thorianite supplied by Professor T. R. Merton, and a specimen of mixed metals from the Urals supposed to contain Ru (44), Rh (45), and Pd (46), supplied by Mr. A. C. E. Egerton.

In addition to those mentioned above our thanks are due to Mr. T. V. Barker and Mr. E. J. Bowen, who supplied us with the minerals used; also to Professor F. A. Lindemann, F.R.S., for his interest and advice during the course of the work.

XVII. *Experiments on the Duration of Impacts, mainly of Bars with Rounded Ends, in elucidation of the Elastic Theory.* By J. E. P. WAGSTAFF, M.A., Fellow of St. John's College, Cambridge, Lecturer in Physics in the University of Leeds\*.

IN a recent paper †, an expression of the form

$$t = (Mr^2/a + B_1 l) v \gamma (83 \cdot 3 \rho^{1/2} / E^{1/2}) \gamma + 1,$$

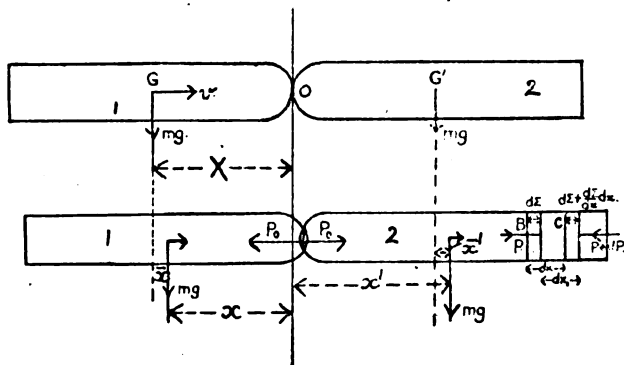
is derived by the method of dimensions for the duration of collision of two perfectly elastic bars. It is now proposed to discuss the form of the mathematical relationships which can account for an expression of this type.

\* Communicated by the Author.

† Proc. Roy. Soc. A. vol. cv. (1924).

Take a system of rectangular axes at O (fig. 1), OG and OG' being the axes of  $x$  for the left-hand bar and the right-hand bar respectively. In the lower figure, the bodies are in a state of compression, the centres of gravity G and G' having moved through distances  $x$  and  $x'$  respectively.

Fig. 1.



If  $P_0$  is the pressure between the bodies at this instant, the equations of motion of the two bars are

$$P_0 = m_0 \frac{d^2 x}{dt^2}, \quad \text{and} \quad P_0 = m_0 \frac{d^2 x'}{dt^2},$$

where  $m_0$  is the mass of either bar.

$$\therefore 2P_0 = m_0 \frac{d^2}{dt^2} (x + x').$$

If  $X$  is the distance of  $G$  and  $G'$  from  $O$  initially,

$$x = X - \bar{x}, \quad x' = X + \bar{x}',$$

therefore  $x + x' = 2X - (\bar{x} - \bar{x}')$ ,

$$\text{so that} \quad 2P_0 = -m_0 \frac{d^2}{dt^2} (\bar{x} - \bar{x}').$$

$\bar{x} - \bar{x}'$  represents the change in the relative position of the centres of gravity of the two bars and may be denoted by  $\alpha$ . The equation thus becomes

$$2P_0 = -m_0 \frac{d^2}{dt^2} \alpha. \quad \dots \dots \dots (I.)$$

In order to obtain a further relationship between  $P_0$  and  $\alpha$ , consider the portion of the bar between planes distance  $dx$

apart initially (fig. 1). If the section at B is displaced a distance  $\Sigma_x$  at the instant the pressure there is P, the section at C is displaced  $\Sigma_x + \frac{d\Sigma_x}{dx} \cdot dx$ , the corresponding pressure being  $P + dP$ .

The equation of motion of the layer is

$$-\frac{dP}{dx} \cdot dx_1 = \rho_1 A_1 dx_1 \frac{d^2 \Sigma}{dt^2},$$

and  $A \rho dx = A_1 \rho_1 dx_1$ , where  $A, \rho, dx$  refer to the cross-section, density, and thickness of the layer in the undisturbed state and the suffixed letters to the corresponding quantities in the disturbed state.

Further assume that at each point of the bar,

$$\frac{d\Sigma}{dt} = VF\left(\frac{d\Sigma}{dx}\right)^*,$$

then

$$P = \rho AV^2 \int \frac{\left\{ F'\left(\frac{d\Sigma}{dx}\right) \right\}^2}{1 + \frac{d\Sigma}{dx}} d\left(\frac{d\Sigma}{dx}\right) = \rho AV^2 \psi\left(\frac{d\Sigma}{dx}\right).$$

In general, an equation of this type indicates a disturbance which is continuously changing its form with time.

If  $F\left(\frac{d\Sigma}{dx}\right) = \frac{d\Sigma}{dx}$ , then  $\frac{d\Sigma}{dt} = -V \frac{d\Sigma}{dx}$ , which is a disturbance of invariable form represented by  $\Sigma = \phi(x - Vt)$  propagated with velocity V.

In particular assume  $\psi\left(\frac{d\Sigma}{dx}\right) = \left(\frac{d\Sigma}{dx}\right)^\beta$  and examine the results to which it leads,

$$-P/A = \rho V^2 \left(\frac{d\Sigma}{dx}\right)^\beta = k \left(\frac{d\Sigma}{dx}\right)^\beta.$$

Such a pressure condensation relationship does not imply any departure from a condition of perfect resilience.

The equation  $-P/A = k \left(\frac{d\Sigma}{dx}\right)^\beta$ , which it is suggested is the form of the stress-strain relationship in the case of impacts of the kind that are here being considered, has the

\* Earnshaw, Phil. Trans. p. 146 (1859).



same type of relation to Hooke's law  $-P/A = k \frac{d\Sigma}{dx}$  as the gaseous law for adiabatic changes  $p = \kappa \rho^\gamma$  has to the isothermal equation  $p = \kappa \rho$ .

Moreover the centre of gravity of the layer is displaced from the origin a distance

$$\Sigma_x + \frac{d\Sigma_x}{dx} \cdot \frac{dx}{2}.$$

The centre of gravity of the right-hand bar is consequently moved through a distance  $\bar{x}'$  given by

$$\bar{x}' = \frac{\rho}{m_0} \int_0^l A \left( \Sigma_x + \frac{d\Sigma_x}{dx} \cdot \frac{dx}{2} \right) dx$$

away from the origin O.

$$\text{If} \quad P/A = -k \left( \frac{d\Sigma}{dx} \right)^\beta,$$

$$\Sigma_x - \Sigma_0 = - \int_0^x (P/Ak)^{1/\beta} dx,$$

$$\text{and} \quad \bar{x}' = \frac{\rho A}{m_0} \int_0^l dx \left( \Sigma_0 - \int_0^x (P/Ak)^{1/\beta} dx \right).$$

Similarly for the left-hand bar,

$$\bar{x} = \frac{\rho A}{m_0} \int_0^l dx \left( \Sigma_0 + \int_0^x (P/Ak)^{1/\beta} dx \right),$$

and

$$\alpha = \bar{x} - \bar{x}' = \frac{2\rho A}{m_0 (Ak)^{1/\beta}} \int_0^l dx \int_0^x P^{1/\beta} dx.$$

If the pressure  $P$  is expressible as a function of  $x/l$ ,  $P^{1/\beta} = f(x/l)$ , the value of the integral

$$\begin{aligned} \int_0^x dx \int_0^x P^{1/\beta} dx &= \int_0^x dx \int_0^x f(x/l) dx, \\ &= l^2 \int_0^t dt \int_0^t f(t) dt \quad \text{where } x/l = t, \\ &= l^2 \left( \int_0^t \{ \phi(t) - \phi(0) \} dt \right) \quad \text{where } \frac{\partial \phi}{\partial t} = f, \\ &= l^2 (\psi(t) - \psi(0) - t\phi(0)) \quad \text{where } \frac{\partial \psi}{\partial t} = \phi. \end{aligned}$$

Again,

$\psi(t) = \psi(0) + t\psi'(0) + t^2\psi''(0)/2! + t^3\psi'''(0)/3! + \dots$ ;  
therefore

$$l^2(\psi(t) - \psi(0) - t\phi(0)) = l^2\left(t^2f(0)/2! + t^3\left(\frac{\partial f}{\partial t}\right)_0/3! + \dots\right),$$

$$= x^2 P_0^{1/\beta}/2! + x^3\left(\frac{\partial}{\partial x} P^{1/\beta}\right)_0/3! + \dots,$$

i. e.  $\int_0^t dx \int_0^x P^{1/\beta} dx = l^2 P_0^{1/\beta}/2! + l^3\left(\frac{\partial}{\partial x} P^{1/\beta}\right)_0/3! + \dots$

Now  $\left(\frac{\partial}{\partial x} P^{1/\beta}\right)_0$ ,  $\left(\frac{\partial^2}{\partial x^2} P^{1/\beta}\right)_0$  and all subsequent differential coefficients are extremely small. For

$$\left(\frac{\partial}{\partial x} P^{1/\beta}\right)_0 = \frac{1}{V}\left(\frac{\partial}{\partial t} P^{1/\beta}\right)_0 \text{ where } \left(\frac{\partial}{\partial t} P^{1/\beta}\right)_0$$

is the rate of variation of the pressure with time at  $x=0$ , and  $V$  is the velocity of sound. • If, as Hertz assumes, impacts are relatively slow processes,  $\left(\frac{\partial}{\partial t} P^{1/\beta}\right)_0$  is small and  $\left(\frac{\partial}{\partial x} P^{1/\beta}\right)_0$  is very much smaller, and similarly for the higher order differential coefficients.

Therefore

$$\int_0^t dx \int_0^x P^{1/\beta} dx = l^2 P_0^{1/\beta}/2,$$

and

$$\alpha = \frac{2\rho A}{m_0(Ak)^{1/\beta}} \cdot \frac{P_0^{1/\beta} l^2}{2}.$$

Writing

$$m_0 = \pi r^2 l \rho,$$

$$P_0 = k\pi r^2 (\alpha/l)^\beta. \dots \dots \dots (II.)$$

Substitute for  $P_0$  in (I.),

$$2k(\alpha/l)^\beta \pi r^2 = -m_0 \frac{d^2 \alpha}{dt^2},$$

multiply by  $2 \frac{d\alpha}{dt}$  and integrate

$$\left(\frac{d\alpha}{dt}\right)^2 + \frac{2k\pi r^2}{m_0 l^\beta} 2 \cdot \frac{\alpha^{\beta+1}}{\beta+1} + \text{constant} = 0.$$

Initially  $\alpha=0$  and  $d\alpha/dt=v$ , therefore  $v^2 + \text{constant} = 0$ ,

i. e.  $\frac{\left(\frac{d\alpha}{dt}\right)^2 - v^2}{2} + \frac{2k\pi r^2}{m_0 l^\beta} \cdot \frac{\alpha^{\beta+1}}{\beta+1} = 0. \dots \dots (III.)$

At the moment of greatest compression  $\frac{d\alpha}{dt} = 0$ . If the value of  $\alpha$  is then  $\alpha_1$ ,

$$\frac{2k\pi r^2}{m_0 l^\beta} \cdot \frac{\alpha_1^{\beta+1}}{\beta+1} = v^2/2.$$

Integrating (III.),

$$\frac{d\alpha}{\left(v^2 - \frac{4k\pi r^2 \alpha^{\beta+1}}{m_0 l^\beta (\beta+1)}\right)^{1/2}} = dt,$$

and the time of impact is given by

$$\begin{aligned} t &= 2 \int_0^{\alpha_1} \frac{d\alpha}{\left(v^2 - \frac{4k\pi r^2 \alpha^{\beta+1}}{m_0 l^\beta (\beta+1)}\right)^{1/2}} \\ &= \frac{2}{v} \left( \frac{v^{2/\beta} m_0 (1+\beta)}{4k\pi r^2} \right)^{1/1+\beta} \int_0^1 \frac{dx}{(1-x^{\beta+1})^{1/2}}. \end{aligned}$$

Writing  $m_0 = \pi r^2 l \rho$  and  $\gamma = 1 + \beta/1 - \beta$ ,

$$t = l \pi^{1/2} v^\gamma \frac{(2/1+\gamma)^{1+\gamma/2} \Gamma(1+\gamma/2)}{4^{1+\gamma/2} \Gamma(2+\gamma/2)} (\rho/k)^{1+\gamma/2}, \quad \text{(IV.)}$$

which is of precisely the same form as that obtained by the method of dimensions.

Assuming that for very long rods  $\gamma \rightarrow 0$ , the time of collision reduces to  $t = 2 \cdot 2 l (\rho/k)^{1/2}$ . Since  $-1/\gamma$  has been found to be expressible in the form  $-1/\gamma = A'' + Kl/r$ ,

$$\beta = \frac{A'' + 1 + Kl/r}{A'' - 1 + Kl/r} = \frac{P + Kl/r}{Q + Kl/r},$$

so that on substitution in equation (II.),

- (a) for long rods  $\beta \rightarrow 1$ , and  $P_0 = k\pi r^2 (\alpha/l)$ ,
- (b) for short rods  $\beta \rightarrow P/Q$ , and  $P_0 = k\pi r^2 (\alpha/l)^{P/Q}$ ,
- (c) for intermediate rods

$$\beta = \frac{P + Kl/r}{Q + Kl/r} \text{ and } P_0 = k\pi r^2 (\alpha/l)^{\frac{P+Kl/r}{Q+Kl/r}}.$$

In (a) the stress strain relationship reduces to Hooke's law, so that the stress can be assumed to be distributed uniformly over the section of the bar; the point source of pressure has lost its identity and the various elements of the original wave have gathered themselves up into a plane wave (compare with the case of a liquid injected into a long narrow tube through a point source at one end).

In (b), on the other hand, the cylindrical boundary exerts no powerful influence on the impact owing to the shortness of the rods. The pressure becomes dissipated through the body and the various elements are not able to reinforce one another and produce a combined wave-front. The rapid dispersion of the stress also explains why, in the spherical problem, Hertz can assume that the whole compression takes place at the point of impact, the remainder of the sphere acting as a rigid body. The problem of two bars each of length  $2r$  does not differ widely from the Hertz problem of two balls of radius  $r$ . If  $P/Q=3/2$ ,

$$P_0 = \pi r^2 k (\alpha/l)^3 = 1.06 r^{1.2} k \alpha^{3.2}.$$

For the problem of two balls, Hertz gives

$$P_0 = .53 r^{1.2} k \alpha^{3.2}.$$

It follows from the foregoing that in the case of two bodies whose lateral dimensions are comparable with the longitudinal ones, the stress is dispersed through the bodies and the energy in consequence is scattered. The presence of a cylindrical boundary introduces the condition that the stress has no normal component at the boundary; the lines of pressure tend to become parallel to the boundary, the stream of energy being guided along the bars. The extent to which this can be accomplished depends on the ease or otherwise with which radial strain can be transformed into longitudinal strain.

$$\text{Now, } \frac{\text{Longitudinal energy at boundary}}{\text{Radial energy at boundary}} = \frac{2\pi^2 m v^2 b^2}{2\pi^2 m v^2 a^2},$$

where  $m$  is the mass of the vibrator,  $v$  its frequency,  $b$  the longitudinal amplitude, and  $a$  the corresponding radial amplitude. If  $l$  is the length of the bar and  $r$  its radius,

$$b/a = dl/dr = \sigma l/r, \text{ where } \sigma \text{ is Poisson's ratio.}$$

The ease or otherwise with which a divergent wave of compression is transformed into a plane longitudinal wave therefore depends on the quantity  $\sigma l/r$  occurring as an index in the expression

$$(P_0/Ak)^{Q+\kappa l/r} = (\alpha/l)^{P+\kappa l/r}.$$

$K$  should thus be proportional to Poisson's ratio.

The case of loaded bars follows from this point of view. Let  $m_0 = \pi r^2 l \rho$  be the mass of the bar and  $M = \pi r^2 l_1 \rho$  the mass of the collar. Then

$$2P_0 = -(M + m_0) \frac{d^2 \alpha}{dt^2},$$

where  $P_0$  is the pressure between the bodies and  $\alpha$  is the

relative movement of their centres of gravity. The pressure  $P_0$  can also be written

$$P_0 = \pi r^2 k (\alpha' / l)^\beta,$$

where  $\alpha'$  is a quantity defined by the equation  $(m_0 + M)\alpha' = m_0 \alpha$ . Substituting for  $\alpha'$ ,

$$P_0 = \pi r^2 k (m_0 \alpha / \overline{M + m_0})^\beta.$$

The law is not obeyed for large initial velocities of approach, as the collar is not able to take up the full movement. The time of impact consequently shows a rapid falling off for large values of  $v$  as indicated in a previous paper.

Alternatively, it has been shown by experiment that in the case of equal bars of radius  $r$ , length  $l$ , and density  $\rho$ , each loaded with a mass  $M$ , the relationship between the time of collision and the relative velocity of approach is of the form  $t = A\gamma$  where  $-1/\gamma = A'' + K(l + l_1)/r$ ,  $l_1$  being given by the equation  $\pi r^2 l_1 \rho = M$ . This generalization of the equation  $-1/\gamma = A'' + K/l$  which applies to simple bars, must follow since the motion of the load is longitudinal. The quantity  $\sigma l/r$  is increased to  $\sigma(\pi r^2 l \rho + M)/\pi r^2 \rho = \sigma(l + l_1)/r$ . This suggests that the case of loaded bars is met if  $l + l_1$  replaces  $l$  in all the formulæ. Thus

$$2P_0 = -(M + m_0) \frac{d^2 \alpha}{dt^2},$$

and

$$P_0 = \pi r^2 k (\alpha / l + l_1)^\beta,$$

which give a time of collision

$$t = \frac{2r^{1-\beta} l^{1+\beta}}{4^{1/l+\beta}} (\beta + 1)^{1+\beta} (\rho/k)^{1+\beta} (l + l_1) \int_0^1 \frac{dx}{(1 - x^{\beta+1})^{1/2}},$$

i. e. the bars have the same time of impact as two bars of the same diameter and material and of such a length  $L$  that  $\pi r^2 L \rho = M + m_0$ . This has been found to be the case.

The suggestion, from these experiments, that the time of impact depends fundamentally on the mass and not on the length of the bars leads to a formula for  $t$  of the form  $t = C(l^{1/3} r^{2/3} \rho/E)^{1/2}$ . The possibilities of this formula have been investigated but it has proved unsatisfactory.

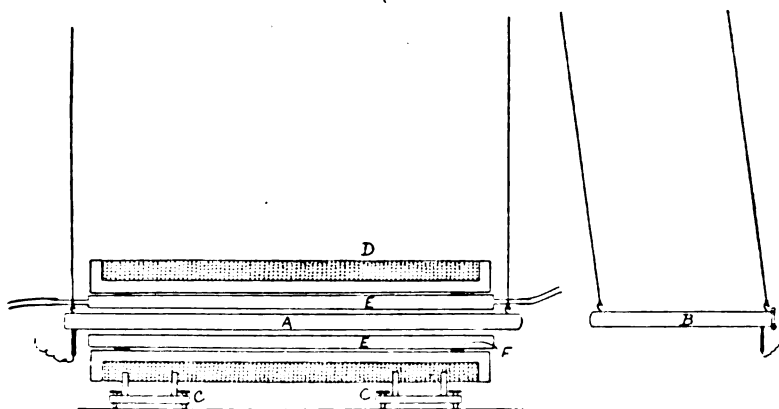
#### *The Effect of a Longitudinal Magnetic Field on the Time of Impact of Steel Bars.*

It seems possible that under the action of a magnetic field the time of impact may be slightly modified since the magnetic properties of iron are molecular in origin.

The arrangement used in the experiment is shown in fig. 2. A steel bar A (61.25 cm. long) is suspended so as to

lie symmetrical with respect to and along the axis of a solenoid D wound round an ebonite cylinder. The solenoid rests on small V-shaped blocks C fitted with levelling screws for adjusting the height. Between the solenoid and the bar is fitted a water-jacket through which a stream of water runs continuously. This prevents any heating of the bar due to conduction. In the light of experience the precaution now seems almost unnecessary, but at the time it was considered desirable to eliminate all spurious effects as completely as possible. E and D are separated by two bands of insulating tape wound round the jacket, and an annular space of  $\frac{1}{4}$  in. separates the jacket and the bar. The solenoid

Fig 2.



needs accurate adjustment. When a current is passed round the solenoid, the bar is in general moved bodily so as to embrace the greatest number of lines of the magnetizing field. This motion can, however, be removed completely by a suitable disposition of the coil. To test this, the rounded end of the bar is viewed broadside on with a microscope and the solenoid is moved about until the end of the bar coincides with the same scale division whether the current is on or off. Any sideways movement is similarly eliminated. In order to get rid of the strong magnetic attraction between A and B which would ordinarily render the experiment impossible (as successive impacts would follow one another so rapidly that the condenser would be discharged completely), B is made of Hadfield's non-magnetic steel.

An ammeter and reversing commutator are arranged in the circuit feeding the solenoid, and to avoid hysteresis

heating the current is obtained from accumulators. Several long sets of observations have been taken, of which a typical one is quoted below.

TABLE I.  
Velocity of bar B at impact = 10.352 cm./sec.

Magnetizing field : gauss.	Galvanometer throw for successive impacts.	Mean galv. throw corrected for damping.
0	130, 130.2, 128.5, 129, 129, 130, 129	130.7
+415	{ 129.5, 128.5, 129.5, 129.3, 129.5, 129, 127, } 129.5, 129.5, 129.3, 128, 129.3	130.45
Between these sets of readings the bars are not allowed to collide.		
-415	{ 130.4, 130.0, 130.2, 130.2, 129.7, 129.2, } 129.2, 129.7, 129.7, 129.2, 129.2, 129.2	130.4

Between these sets of readings the bars are not allowed to collide.

0	{ 128, 130.2, 129.2, 127.2, 128.2, 128.2, 135.7 } { 129.2, 129.2, 136.7, 136.2, 129.7, 129.9, 129.2, } { 129.2, 130, 125.7, 128.2, 126.2, 129.2, 128.7, } { 129, 129.2, 129.2, 125.2, 128.7, 128.7, 128.7, } { 129.2, 129.2, 135.7, 129.5, 129.5, 128, 129.5, } { 129.5, 130.3, 130.2, 127.7, 129.7, 129.7, 128.5, } { 128.2, 129.7, 129.7, 129.7, 129.2, 128, 128.2, } { 128.2, 133.7, 129.2, 129.2, 130, 129.7, 129.7, } { 129.7, 129.7, 129.2, 129.2, 129.4, }	130.5
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An interval of twelve hours occurs here, but the surfaces of the bars are not touched before proceeding with the following.

0	{ 128.5, 128.5, 130, 129, 129.3, 129, 129.5, 129.5, } { 129.5, 129, 129, 129.5, 129, 129, 129.5, 129, } { 129.3, 128.5, 129, 129.5, 129, 129, 129, 129.3, } { 128, 129.5, }	130.5
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The bar A is now completely demagnetized and a long set of readings is taken to test their constancy.

0	{ 132, 131.8, 131.8, 131.0, 131.0, 132.0, 131.0, } { 131.5, 131, 131.5, 131, 131.5, 131.2, 132, 131, } { 131, 131, 131.5, 131, 131, 131, 131, 131.5, } { 130.5, 130.5, 130.5, 131, 131, 130.5, 130.5, } { 131, 130.8, 130.5, 130.5, 130.5, 130.3, 131, } { 130.5, 130.5, 130.5, 131, 130.8, 130.8, 130.3, } { 130.3, 130.8, 130.8, 130.5, 130.8, 130, 130.3, } { 131, 130.5, 130.8, 130.3, 131, 130.8, 130.5, } { 130.8, 130.8, 130.5, 130.8, 130.3, 130.3, 130.5, } { 130.5, 131, 130.8, 131, 130.5, }	132.3
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The above readings, which were taken with extreme care, show that the average values for the magnetized state are the same as for the demagnetized state. They do, however, exhibit quite an interesting effect. On examining sets 1 and 2 of the above table, it is seen that the individual readings vary very little about the mean. On the other hand, the second impact of set 3 (corresponding to the reversal of the magnetizing field together with the delivery of one previous blow to the bar) is abnormally short, after which they are steady again.

In set 4, taken immediately after switching off the magnetizing field, the 2nd, 4th, 7th, 10th, 11th, 17th, 19th, 26th, 32nd, and 52nd impacts are short, after which they are comparatively steady.

It is suggested that the erratic readings do actually reflect a change in the state of the metal due to the blow delivered at the end. Changes of the order observed can be produced by the slight stretching of a suspension, a slight departure from perfect alignment, or the presence of a speck of dust at the place of impact. The impacts immediately preceding or following these abnormal ones are, however, perfectly normal usually, which would not be the case if the effects were due to any of the alternative explanations given above. In the latter case a permanent change of reading would result.

In order to pursue the inquiry whether the abnormal readings can be taken to indicate an internal change as opposed to a variation in external conditions, several extended series of observations were taken with the same bars after demagnetization, and for zero magnetizing field. One series of seventy consecutive readings is given in Table I. It is seen that there is not a single abnormal impact. There is a tendency for the impacts to get progressively shorter, but this can be traced to a change in the external conditions, viz. a gradual flattening of the end of the non-magnetic steel bar.

The abnormal impacts are therefore probably due to a change in the magnetic state of the bar produced by the blow on the end. It has previously been shown that the duration of impact is related to the initial velocity of approach by the equation  $t = A\epsilon v$ . The kinetic energy of the impinging bar at the instant of impact  $= \frac{1}{2}m_0v^2$ . If it is legitimate to assume that this energy, during impact, represents the energy of the waves of compression passing through the bars

$$t = \text{constant}/(\text{Energy in compression wave})^{-1/2}.$$

Any change in the energy will be reflected in the duration of the impact. The short impacts may indicate that the



wave while passing through the bar has become enriched in energy due to the breaking up of aggregates peculiar to the magnetized state into aggregates corresponding to the normal state.

*The Effect of Temperature on the Time of Impact of Steel Bars.*

This short series of experiments sets out to determine the effect of temperature on the duration of impact. From the small effects obtained, it is clear that the results of the experiments on the effects of a magnetizing field, described in the last section, are in no way associated with temperature variations in the bars.

For this investigation each bar is provided with a steam-jacket from which it is insulated by thin ebonite plugs, and the times of impact are found at 18° C. and 100° C. The results are given below.

TABLE II.

Temperature of bar.	Resistance in circuit: ohms.	Galvanometer throw.	Mean value of throw.
18° C.	187	{ 189, 189.5, 189.5, 189, 189.5, 189, } 189.5, 189.5, 189, 189.5	189.3
	287	{ 154.2, 154, 154.2, 153.5, 153.8, } 154.5, 154, 154	154.03
	387	{ 130.5, 130.2, 130, 130, 131, 131, } 131, 130.5, 131.5, 131	130.67
	687	90, 90, 90, 90, 90, 89.5	89.92
99.5° C.	187	{ 189.5, 189.5, 189, 189.5, 189.5, } 189.5, 189.5	189.43
	287	{ 154.5, 154.5, 154.5, 154.2, 154.5 } 154.7, 154.7	154.52
	387	131, 130, 131, 131, 130.3	130.66
	687	90, 90, 90, 90, 89.5	89.92

The readings at 18° C. seem to be slightly less than those at 100° C., indicating that the duration of impact is slightly less at the lower temperature, but on the whole the change is quite negligible.

In conclusion, I wish to thank Mr. C. Barnes, M.Sc., for his assistance in the experimental portions of the paper, and to thank also the Grants' Committee of the Royal Society for defraying the cost of the apparatus.

University of Leeds.  
August 31st, 1923.

XVIII. *The Emission Spectra of Mixed Alkali Vapours.*  
 By F. H. NEWMAN, D.Sc., A.R.C.S., Professor of Physics,  
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(Plate IV.)

1. *Introduction.*

IN a previous paper † the author has described an emission continuous spectrum which is obtained when an electric arc is passed between two pools of the alloy of sodium and potassium. The spectrum consists of two parts—one in the red region and the second in the blue-green region, the former being by far the more intense. Another interesting feature was the formation of an emission fluting spectrum, the heads of the bands being situated between the limits  $\lambda 6700$  and  $\lambda 5500$ . These results have been studied in greater detail in the present experiments.

The absorption by sodium vapour is of two types, a principal series which is characterized by the empirical formula of the emission principal series of which the D lines form the first member. In addition, there are a number of very complicated channelled absorption bands which do not seem to influence dispersion. One of these bands lies in the red,  $\lambda 5800$  to the extreme limit of the visible red, and the other in the blue-green region,  $\lambda 5700$ – $\lambda 4500$ , though with dense vapour they practically meet in the yellow. Wood ‡ has found that there are about 6000 absorption lines in these bands in the visible region, and the regions transmitted between the absorption lines are as narrow apparently as the emission lines of the iron arc. There are on an average 60–70 absorption lines within a space of only 12 Angström units in width. These lines, taken collectively, form themselves into a number of groups which resemble the groups seen in the absorption spectra of iodine and bromine, and in certain banded emission spectra. Although there are no actual emission spectra corresponding to the complicated absorption ones, Wood has shown that these bands are connected with the fluorescent spectra; and probably when sodium vapour is illuminated with a powerful beam of white light, its fluorescent spectrum is the exact complement of the absorption spectrum. If the vapour is stimulated with monochromatic light, a series of bright lines spaced at nearly equal intervals along a normal spectrum and separated by a distance

\* Communicated by the Author.

† Phil. Mag. xlv. (September 1923).

‡ 'Physical Optics,' 1911.

equal to 37 Ångström units is obtained. Various series of lines can be made prominent by altering the wave-length of the exciting light. Stimulation by  $\lambda$  4800 from the cadmium arc produces a series of bright lines spaced at nearly equal intervals along a normal spectrum. The bismuth arc produces a resonance spectrum consisting of a series in the blue which with long exposures can be traced well up into the green, and a large number of lines in the yellow-green part of the spectrum. With the lithium arc, definite series of lines can be excited in the red region, and the four exciting lines all produce different lines in the resonance spectrum.

The existence of bands with sodium vapour is due to associated atoms of the alkali vapour. The pure rotation band-spectra, as observed by Rubens\* with water vapour, can be explained by the change in the rotational quantum number by  $\pm 1$ . Bands in the visible region occur when there is a change in the configuration of the molecule which results in a decrease in the internal energy at the same time as the change in angular momentum. This change of configuration of molecule consists in a re-arrangement of the electrons or the atoms within the molecule.

If the dispersion of the instrument is not sufficient, some band-spectra appear continuous, especially those which consist of the so-called many-line spectra. In addition, there are really continuous spectra both in emission and absorption. This continuous character is especially marked in the case of the absorption bands observed with sodium vapour. There is a selective absorption in a continuous spectrum region beginning at the limit of the principal series and extending into the ultra-violet. This confirms the assumption that the absorption of energy corresponding to lines in the principal series of sodium results in fixed states of the atom in which one of the electrons revolves in larger and larger orbits. This continuous absorption corresponds to transitions from the normal state to states in which the electron is in a position to remove itself infinitely far from the nucleus. A continuous spectrum arises if an originally free electron is taken up into the configuration of an originally ionized atom and the latter is neutralized.

In the case of iodine, Steubing† has photographed an emission spectrum of iodine which appears as a continuous band, even at dispersions that completely resolve the very narrow band-spectrum of iodine. The atom of the latter tends to perfect the 8-shell arrangement by taking a free

\* *Berliner Ber.* 1913, p. 513.

† *Zeitschrift für Phys.* v. (1921).

electron, and as a result it is highly electronegative in properties. Hence, it need not be ionized to attract an electron to itself, but the electron affinity suffices to effect the taking up of the free electron.

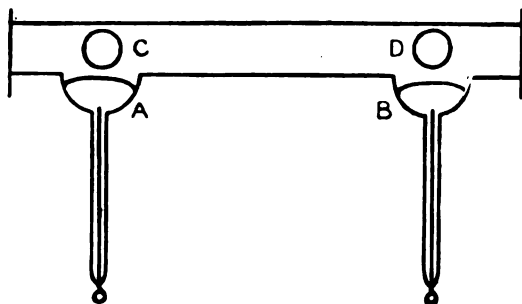
Wood found that potassium vapour has a channelled absorption spectrum consisting of more or less regularly-spaced bands lying within the orange-red region limited by  $\lambda$  6346 and  $\lambda$  6667, and McLennan and Ainslie \* have shown that, in addition to these bands, there is a series of fine channelling beyond  $\lambda$  7699 towards the infra-red, and bands in the neighbourhood of  $\lambda$  4273 when vapour of high density is used. Vapours of the other alkali metals also exhibit channelled absorption bands.

It is to be expected that when we are dealing with mixed vapours of more than one alkali there will be bands due to each element, and in addition bands due to the association of atoms from the different elements.

## 2. Experimental Results.

The form of quartz tube used in the present work is shown in fig. 1. Sodium potassium alloy—equal parts by weight of

Fig. 1.



sodium and potassium—formed the two electrodes at A and B. The ends of the tube were closed with glass plates cemented with wax, and C and D were two side-tubes, so that the spectra immediately at the anode and cathode could be observed, and photographed on panchromatic plates with a constant deviation type of spectrometer. The arc could be readily maintained with an applied potential difference of 50 volts, and the current was controlled by a variable resistance in series with the tube. Sometimes the arc was started by warming the tube with a bunsen flame; otherwise

\* Proc Roy. Soc. ciii. (1923).

it was necessary to apply a discharge from an induction coil in addition. Once started, the lamp required no further attention, there being no gases liberated. The heat produced by the current was sufficient to produce the requisite vapour-pressure, but for high vapour-pressures a coil of nichrome wire wound round the tube was heated electrically.

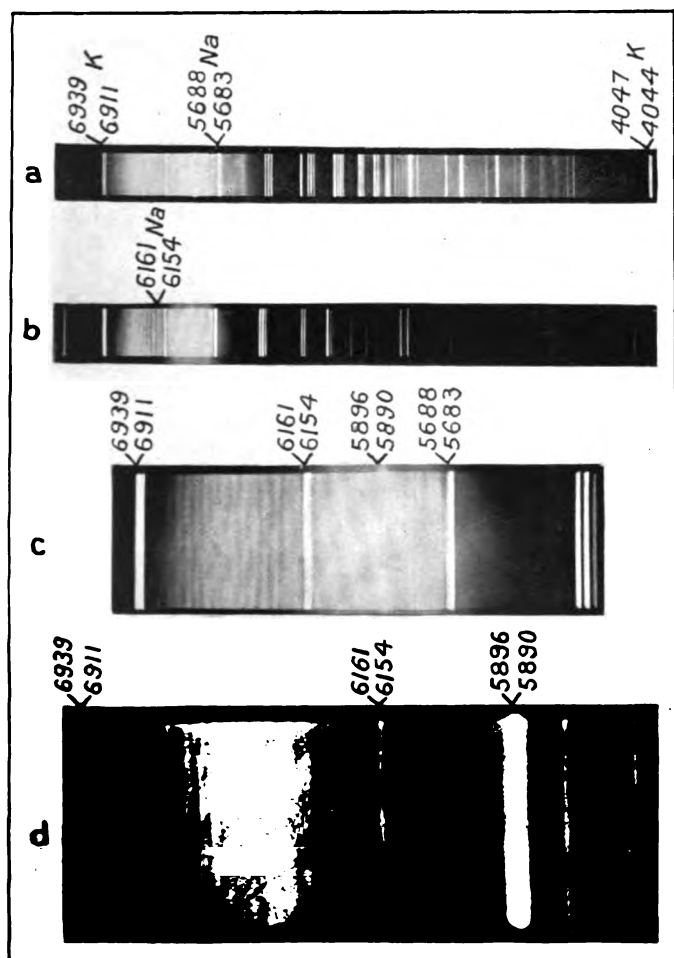
In addition to the well-known series of sodium and potassium lines, there were exhibited the bands previously observed. With small vapour-pressures they were faint, increasing in brightness as the tube was heated or the current increased. The increased intensity is due to the greater vapour-pressure. As the latter was raised, the bands merged into a continuous band which extended from  $\lambda$  6780 to  $\lambda$  5485. In addition, at higher temperatures another band which appeared continuous between the limits  $\lambda$  4750,  $\lambda$  4040 was exhibited. This latter band was noted when the alloy was heated to  $300^{\circ}\text{C}$ ., although it is difficult to estimate the actual temperature within the tube. It is certain that this temperature exceeds that registered by a thermometer placed within the electric heater. The admission of a little nitrogen or hydrogen to the lamp caused the appearance of the band in the red region, suggesting that the total pressure within the tube decides the formation of this band.

The instrument used was not of sufficient dispersive power to examine the structure of the individual bands constituting the channelling in the red, but they were slightly degraded towards the blue. These bands extended from  $\lambda$  6776 to  $\lambda$  5931, but from  $\lambda$  5931 to  $\lambda$  5485 merged into a continuous band which could not be resolved. Unfortunately, the intense radiation emitted by the D lines of sodium prevented observation of the wave-lengths in the immediate neighbourhood of  $\lambda$  5893 (Pl. IV.).

The series of bands in the red region which formed a channelled spectrum were measured, and gave the mean wave-lengths recorded in Table I.

The continuous band in the green-blue probably consists of a large number of bands. At low vapour-pressures they are too faint to be observed, and merge into the continuous band at higher pressures. This seems to show that, with the vapour at moderate density, only a small proportion of the vapour is in the molecular state suitable for giving this particular type of emission.

It is probable that the complete banded spectrum arises from three distinct sets of molecules—viz., potassium, sodium, and molecules consisting of associated atoms of both elements. The sodium and potassium arcs are difficult to regulate, and



Emission Banded Spectra of the Vapour from  
Sodium-Potassium Alloy.



it was impossible to detect banded emission-spectra from these elements separately.

TABLE I.

$\lambda$ A.U.	$\nu$ = Frequency.	$c\nu$ .
5931	16861	130
5977	16731	111
6017	16620	124
6062	16496	127
6109	16369	
6161 Na line	16231	
6154 Na line	16250	
6193	16147	101
6232	16046	130
6283	15916	118
6330 †	15798	104
6372 †	15694	121
6420 †	15573	98
6462	15475	97
6503	15378	80
6537	15298	93
6577	15205	104
6622	15101	108
6670	14993	116
6722	14877	119
6776	14758	

† Sharp.

### 3. Description of Plate IV.

- (a) Continuous band from  $\lambda$  6780 to  $\lambda$  5485, and from  $\lambda$  4750 to  $\lambda$  4040.
- (b) Channelling consisting of bands from  $\lambda$  6776 to  $\lambda$  5931, and a continuous band from  $\lambda$  5931 to  $\lambda$  5485.
- (c) An enlarged spectrogram of a part of (b), showing the bands in the red region.
- (d) Bands in the red region, the vapour-pressure being greater than in (c).



**XIX. *The Motion of a Rigid Solid according to the Relativity Principle.* By G. LEMAÎTRE, D. ès Sc. (Louvain) \*.**

[SINCE previous work on M. Lemaitre's problem—intermediate between the special and general relativity theories—is probably not very familiar to English readers, a brief introduction may be desirable. Simultaneity is relative: but relative to what? In the special theory it is relative to a uniformly moving particle, it being assumed that we have a means of fixing constant orientation in space—or, to combine the two conditions, relative to a "Galilean" frame of axes. If we seek to materialise the Galilean frame, we must substitute a rigid solid. Now an actual solid of reference may differ from a Galilean frame, either because it is rotating or because its motion as a whole is accelerated (by non-gravitational forces). This invites a generalization of the definition of simultaneity, so that we may consider simultaneity relative to a generally moving solid. We still limit ourselves to a particular case of the general theory, because our four-dimensional continuum of space-time is assumed to be flat (Euclidean); but, as M. Lemaitre shows, in certain cases the resolution into space and time separately gives a three-dimensional space which is curved. By studying this transition we see how the notion of simultaneity gradually fades out in passing from the special to the general theory: in motions of class A, it remains definite but is no longer a matter of permanent adjustment of clocks; in motions of class B, it exists only between neighbouring points and becomes ambiguous for distant points unless a route of connexion is specified. The definition of a rigid body appeals to space-measures: but simultaneity is involved in the separation of space-measures from time-measures; and simultaneity in its turn is relative to the rigid body. It is of interest to note how this logical tangle is approached.—A. S. EDDINGTON.]

1. **T**HE variable motion of a solid and the correlative aspects of phenomena for moving observers is an intermediate problem between the first relativity theory of uniform motion and the general principle by which gravitation is accounted for.

The fundamental paper on this question is that of M. Born †, who has fixed the general meaning of the interval and its spatio-temporal interpretation as retained in the general theory. The necessity of throwing over the Euclidean Geometry in Born's conception has been pointed out by Ehrenfest ‡. Finally, G. Herglotz § has investigated

\* Communicated by Prof. A. S. Eddington, F.R.S.

† *Ann. d. Phys.* xxx. p. 1 (1909).

‡ *Phys. Zeitschr.* x. p. 918 (1909).

§ *Ann. d. Phys.* xxxi. p. 393 (1910).

the most general possible movement of a solid in a Galilean field. We will summarize these results and deduce developments and applications suggested by the present point of view of the Relativity Theory.

All physical notion of space and time may be expressed by measures of *interval* or generalized length of lines in the four-dimensional Universe. The time of a chronometer (proper time) is the interval along its line of universe.

Simultaneity as defined by light-signals observed on a definite body is such that the direction of a line of simultaneity is conjugate to the direction of the lines of universe described by the body with respect to the light-cone, or locus of vanishing intervals, passing through the point.

In the geometrical interpretation, lines of simultaneity are orthogonal trajectories of the lines of universe described by the body.

A spatial length on a body is the interval along its lines of simultaneity.

In the particular case ordinarily considered there is a definite set of point-events which can be joined to a given point-event by lines of simultaneity. In this case it is possible to assign to this set of points a number which is called the *time of simultaneity* on the body. All the point-events of same time of simultaneity, and only these, can be joined by lines of simultaneity. The definition of simultaneity does not depend on the path by which it is defined; its mathematical expression is an exact differential, and it may therefore be used as a coordinate.

But in the general case it is possible to draw a line of simultaneity through any two arbitrary point-events, and there is no possible definition of a time of simultaneity. Examples of this will be given below.

Now a rigid solid is a body on which all the relative spatial distances of points, measured on the body, are left unaltered by the movement. It must be observed that the definition of spatial distance refers only to the line of simultaneity and is independent of the existence of a time of simultaneity.

The possible movements of a solid have been divided by Herglotz into two classes according to the existence of a time of simultaneity or not. The movements of class A, *i. e.* with a time of simultaneity, are completely determined by the arbitrary motion of one point.

In this case the interval can be written, by a convenient

choice of coordinates, in the form

$$ds^2 = -dx^2 - dy^2 - dz^2 + \phi^2 dt^2, \quad . \quad . \quad . \quad (1)$$

where  $\phi$  is a function of  $x, y, z, t$ .

In the movements of class B, the motion of every point must be expressed by use of a parameter which is not a time of simultaneity. This parameter may be chosen so that the interval between two arbitrary points is not altered when the same number is added to their respective parameters. The line of universe described by every point is transformed into itself by the movement, and the general movement of class B is a one-parameter group of movements in the Universe.

On the basis of these results of Herglotz we begin by investigating movements of class A for which the given motion of a point is rectilinear.

## 2. Rectilinear movement.

Let  $v$  be an arbitrary function of  $t$  whose derivative is  $g$ . Then

$$\left. \begin{aligned} d\xi &= \cosh v \, dx + (1 + gx) \sinh v \, dt, & d\eta &= dy, & d\zeta &= dz, \\ d\tau &= \sinh v \, dx + (1 + gx) \cosh v \, dt, \end{aligned} \right\} \quad (2)$$

are the exact differentials of the functions

$$\left. \begin{aligned} \xi &= x \cosh v + \int \sinh v \, dt, & \eta &= y, & \zeta &= z, \\ \tau &= x \sinh v + \int \cosh v \, dt, \end{aligned} \right\} \quad . \quad . \quad (3)$$

which define a transformation from the coordinates  $\xi, \eta, \zeta, \tau$  to  $x, y, z, t$ .

The interval in a Galilean field

$$ds^2 = -d\xi^2 - d\eta^2 - d\zeta^2 + d\tau^2 \quad . \quad . \quad . \quad (4)$$

is transformed into

$$ds^2 = -dx^2 - dy^2 - dz^2 + (1 + gx)^2 dt^2. \quad . \quad (5)$$

For given values of  $x, y, z$  the equations (3) define an arbitrary movement of a point of the solid, parallel to the  $\xi$  axis. Equation (5) is thus the general expression of rectilinear movements of class A.

It is easy to see that  $t$  is truly a time of simultaneity. The directions for which  $dt = 0$  are conjugate to the direction

$dx=dy=dz=0$  of the lines of universe of the moving points with regard to the light-cone  $ds=0$ .

The spatial distance is

$$d\sigma^2 = dx^2 + dy^2 + dz^2,$$

obtained by putting  $dt=0$  in the expression of  $ds^2$ .

The time shown by the chronometers of the moving system (proper time) is

$$\int_{t_1}^{t_2} (1+gx) dt = t_2 - t_1 + x(v_2 - v_1). \quad (6)$$

Measures of simultaneity (by light-signals) will show a variable difference between the simultaneous readings of the chronometers. The difference between the time measured by the chronometers from the epoch  $t_1$  to the epoch  $t_2$  at two points of coordinates  $x$  and  $x + \Delta x$  is

$$(v_2 - v_1)\Delta x, \quad (7)$$

which depends on the values of  $v$  at the epochs only.

$v$  is connected with the velocity  $V$  of the system by the relation

$$V = \frac{d\xi}{d\tau} = \tanh v, \quad (8)$$

which is obtained by putting  $dx=0$  in (2).

Conversely,

$$v = \frac{1}{2} \log \frac{1+V}{1-V}. \quad (9)$$

The velocity does not depend on  $x$ . That means that every point has the same speed at the same time  $t$ : i.e., simultaneously for the moving system. For the fixed system, on the contrary (time  $\tau$ ), the speed is taken up progressively so that the length may be altered according to the Lorentz contraction, variable with the variable velocity.

An interesting application may be made to the problem of the change of velocity of a Galilean observer. Suppose that before the time  $t_1$  the velocity has a constant value  $V_1$  corresponding to  $v_1$ , and then varies in amount but keeping the same direction, and finally remains constant after the time  $t_2$ .

Since the system is a Galilean one, before the epoch  $t_1$

the chronometers are able to show the time of simultaneity. During the change of speed ( $t_1, t_2$ ) the simultaneity will be disturbed and, after  $t_2$ , the chronometers will show a constant difference between their simultaneous readings.

This difference is given by (7) and is

$$(v_2 - v_1)\Delta x = \frac{\Delta x}{2} \log \frac{1 + V_2}{1 - V_2} \cdot \frac{1 - V_1}{1 + V_1} \quad (10)$$

$\Delta x$  is the distance measured in the sense of the movement.  $V_1$  and  $V_2$  are the starting and final velocities, the velocity of light being taken as unit. The law of velocity variation is immaterial.

### 3. Movement with constant acceleration.

When  $g$  is a constant, it is possible to carry out the integrations in the transformation (3). Then it may be written :

$$\left. \begin{aligned} 1 + g\xi &= (1 + gx) \cosh gt, \\ g\tau &= (1 + gx) \sinh gt. \end{aligned} \right\} \quad (11)$$

By elimination of  $t_1$  we obtain the equations of the movement

$$(1 + g\xi)^2 - (g\tau)^2 = (1 + gx)^2, \quad (12)$$

or, changing the origin,

$$\xi^2 - \tau^2 = x^2. \quad (13)$$

This is Born's hyperbolic movement. The moving points describe concentric hyperbolas in the plane  $\xi\tau$ .

The interval (5) may be simplified by using new co-ordinates \*

$$ds^2 = -dx^2 - dy^2 - dz^2 + x^2 dt^2. \quad (14)$$

The acceleration of a free point, or geodesic line of the universe, is

$$\frac{d^2x}{ds^2} = -x \left( \frac{dt}{ds} \right)^2, \quad \frac{d^2y}{ds^2} = 0, \quad \frac{d^2z}{ds^2} = 0. \quad (15)$$

The trajectory is a plane and we have for convenient choice of the coordinates

$$ds = \lambda dy, \quad dz = 0.$$

\* This formula is given by Pauli, 'Relativitätstheorie,' p. 648.

Then from (14)

$$x^2 \left( \frac{dt}{dy} \right)^2 = 1 + \lambda^2 + \left( \frac{dx}{dy} \right)^2, \quad . \quad . \quad . \quad (16)$$

and from (15)

$$x \frac{d^2 x}{dy^2} + \left( \frac{dx}{dy} \right)^2 + 1 + \lambda^2 = 0$$

or

$$\frac{d}{dy} \left( x \frac{dx}{dy} \right) + 1 + \lambda^2 = 0.$$

The solution may be written ( $a, b, c$  constant) :

$$\begin{aligned} & \left. \begin{aligned} x &= a \cos \theta, \\ y &= b \sin \theta + c, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (17) \\ \text{with} \quad & \frac{a^2}{b^2} = 1 + \lambda^2. \end{aligned}$$

The trajectories are ellipses with minor axis in the plane  $x=0$ . The time  $t$  is given from (16) by

$$t - t_0 = \int_{\theta_0}^{\theta} \frac{d\theta}{\cos \theta} = \log \frac{\tan \left( \frac{\pi}{4} + \frac{\theta}{2} \right)}{\tan \left( \frac{\pi}{4} + \frac{\theta_0}{2} \right)}. \quad . \quad . \quad (18)$$

When  $\lambda=0$ ,  $ds=0$ , the trajectories are rays of light. They are circles with centre on  $x=0$ .

For comparison with the Schwarzschild-Einstein formula for the field of a particle, it is convenient to effect the transformation

$$(1 + gx)^2 = 1 + 2gX. \quad . \quad . \quad . \quad (19)$$

Then the equation of the field may be written ( $g$  constant) :

$$ds^2 = - \frac{dX^2}{1 + 2gX} - dy^2 - dz^2 + (1 + 2gX) dt^2. \quad . \quad (20)$$

#### 4. General movement of Class A.

It is easy to find the general expression of the function  $\phi$  of  $x, y, z, t$  in Herglotz's equation of a field of class A :

$$ds^2 = -dx^2 - dy^2 - dz^2 + \phi^2 dt^2. \quad . \quad . \quad (21).$$

The necessary condition that this expression is reducible by a change of coordinates to the Galilean form is that the

Riemann tensor vanishes. Its components which do not vanish identically are :

$$B_{ik14} = B_{44ik} = -B_{i4k4} = -B_{4ik4} = \phi \frac{\partial^2 \phi}{\partial x_i \partial x_k}, \quad (i, k = 1, 2, 3), \quad (22)$$

where  $x_1, x_2, x_3$  are written for  $x, y, z$ .

Derivatives with regard to  $t$  do not occur.

$\phi$  must be of the form :

$$\phi = lx + my + nz + p,$$

where  $l, m, n, p$  are functions of  $t$  and the field of a moving system of class A is of the form

$$ds^2 = -dx^2 - dy^2 - dz^2 + (lx + my + nz + p)^2 dt^2. \quad (23)$$

$p$  may be taken equal to one by a change of the co-ordinate  $t$ .

The transformation may be written as follows :

$$\left. \begin{aligned} \xi &= a_{11}x + a_{12}y + a_{13}z + \int a_{14}dt, \\ \eta &= a_{21}x + a_{22}y + a_{23}z + \int a_{24}dt, \\ \zeta &= a_{31}x + a_{32}y + a_{33}z + \int a_{34}dt, \\ \tau &= a_{41}x + a_{42}y + a_{43}z + \int a_{44}dt, \end{aligned} \right\} \quad (24)$$

where the 16 coefficients are functions of  $t$  defined by the 16 differential equations :

$$\left. \begin{aligned} \frac{a'_{11}}{a_{14}} &= \frac{a'_{21}}{a_{24}} = \frac{a'_{31}}{a_{34}} = \frac{a'_{41}}{a_{44}} = l \equiv l_1, \\ \frac{a'_{12}}{a_{14}} &= \frac{a'_{22}}{a_{24}} = \frac{a'_{32}}{a_{34}} = \frac{a'_{42}}{a_{44}} = m \equiv l_2, \\ \frac{a'_{13}}{a_{14}} &= \frac{a'_{23}}{a_{24}} = \frac{a'_{33}}{a_{34}} = \frac{a'_{43}}{a_{44}} = n \equiv l_3, \\ a'_{1\sigma}a_{14} + a'_{2\sigma}a_{24} + a'_{3\sigma}a_{34} - a'_{4\sigma}a_{44} \\ + a_{1\sigma}a'_{14} + a_{2\sigma}a'_{24} + a_{3\sigma}a'_{34} - a_{4\sigma}a'_{44} &= 0, \\ (\sigma &= 1, 2, 3, 4) \end{aligned} \right\} \quad (25)$$

with initial values satisfying

$$\left. \begin{aligned} a_{1\sigma}^2 + a_{2\sigma}^2 + a_{3\sigma}^2 - a_{4\sigma}^2 &= \begin{cases} 1 & \text{for } \sigma = 1, 2, 3, \\ -1 & \text{for } \sigma = 4, \end{cases} \\ a_{1\sigma}a_{1\tau} + a_{2\sigma}a_{2\tau} + a_{3\sigma}a_{3\tau} - a_{4\sigma}a_{4\tau} &= 0 \\ (\sigma \neq \tau &= 1, 2, 3, 4). \end{aligned} \right\} \quad (26)$$

These initial values are possible as they correspond to a Lorentz transformation.

Let us differentiate these equations (26), and observe that for  $\sigma$  or  $\tau=4$  the differential is null by (25) and for  $\sigma, \tau \neq 4$

$$\begin{aligned} & a_{1\sigma} a'_{1\tau} + a_{2\sigma} a'_{2\tau} + a_{3\sigma} a'_{3\tau} - a_{4\sigma} a'_{4\tau} \\ &= l_{\tau} (a_{1\sigma} a_{14} + a_{2\sigma} a_{24} + a_{3\sigma} a_{34} - a_{4\sigma} a_{44}) = 0. \end{aligned}$$

We see that the initial conditions (26) are verified everywhere.

Then

$$d\xi = a_{11} dx + a_{12} dy + a_{13} dz + (a'_{11} x + a'_{12} y + a'_{13} z + a_{11}) dt,$$

and from the above conditions

$$\begin{aligned} & -d\xi^2 - d\eta^2 - d\zeta^2 + d\tau^2 \\ &= -dx^2 - dy^2 - dz^2 + (lx + my + nz + 1)^2 dt^2. \quad (23 \text{ bis}) \end{aligned}$$

Observe that from (26)

$$a_{\sigma\tau} = a_{\tau\sigma}.$$

We will now verify that the movement of one point may be taken arbitrarily. For  $x=y=z=0$ , we have  $ds=dt$  and the velocity of the point is

$$\frac{d\xi}{ds} = a_{14}, \quad \frac{d\eta}{ds} = a_{24}, \quad \frac{d\zeta}{ds} = a_{34}, \quad \frac{d\tau}{ds} = a_{44},$$

with

$$a_{14}^2 + a_{24}^2 + a_{34}^2 - a_{44}^2 = -1.$$

The functions  $l, m, n$  of  $t=s$ ,

$$l = \frac{1}{ds} \frac{d^2 \xi}{d\tau ds^2}, \quad m = \frac{1}{ds} \frac{d^2 \eta}{d\tau ds^2}, \quad n = \frac{1}{ds} \frac{d^2 \zeta}{d\tau ds^2}; \quad (27)$$

may be determined for an arbitrary motion of the point  $x=y=z=0$ .

For every point we have

$$u = \frac{d\xi}{d\tau} = \frac{a_{14}}{a_{44}}, \quad v = \frac{d\eta}{d\tau} = \frac{a_{24}}{a_{44}}, \quad w = \frac{d\zeta}{d\tau} = \frac{a_{34}}{a_{44}}, \quad (28)$$

with

$$a_{44} = (1 - u^2 - v^2 - w^2)^{-\frac{1}{2}} = (1 - V^2)^{-\frac{1}{2}}. \quad (29)$$



*Change of velocity for a non-rectilinear movement.*

The proper time shown by chronometers of the moving system between two epochs  $t_1$  and  $t_2$  is

$$\int_{t_1}^{t_2} (lx + my + nz + 1) dt = t_2 - t_1 + \int \frac{1}{a_{44}} (a'_{41}x + a'_{42}y + a'_{43}z) dt. \quad (30)$$

The difference of the time measured by two chronometers between the two epochs generally depends on the particular law of velocity variation. We have seen that the difference is independent of this law when the velocity keeps the same direction. The same thing happens when  $a_{44}$  is a constant, *i. e.* when  $V$  is a constant. Then the change is

$$\frac{1}{\sqrt{1-V^2}} [(u_2 - u_1)\Delta x + (v_2 - v_1)\Delta y + (w_2 - w_1)\Delta z]. \quad (31)$$

The difference of the simultaneous readings of two chronometers after a change of direction with constant speed does not depend on the described curve but is proportional to the distance of the chronometers and to the difference of the projections of the starting and final velocities on the line which joins them.

*Acceleration of free points.*

Equations of the geodesics are

$$\frac{d^2x}{ds^2} = -l(lx + my + nz + 1) \left( \frac{dt}{ds} \right)^2$$

or

$$\frac{d^2x}{ds^2} = -\frac{l}{lx + my + nz + 1} \left[ 1 + \left( \frac{dx}{ds} \right)^2 + \left( \frac{dy}{ds} \right)^2 + \left( \frac{dz}{ds} \right)^2 \right], \quad (32)$$

and analogous expressions in  $y$  and  $z$ .

As they do not contain derivatives of  $l, m, n$ , the acceleration is the same as if  $l, m, n$  were constant, *i. e.* as in the hyperbolic movement. We have found in this case the law of elliptic motion expressed by the equations (17) and (18) which may be applied with a change of orientation of the axis. These ellipses are in planes perpendicular to the plane  $lx + my + nz + 1 = 0$ , and their small axis is in this plane. They are osculatory to the actual movement.

For rays of light, the ellipses are circles. The osculatory plane of the trajectory is at every instant  $t$  perpendicular to

the moving plane  $lx + my + nz + 1 = 0$ , and the centre of curvature is in this plane.

### 5. Movements of Class B.

In the movements of class A it was possible to find in the moving system a time of simultaneity: *i. e.*, to give the same coordinate to all the points simultaneous with one another. We proceed to the case where this is impossible. Two arbitrarily given point-events may then be considered as simultaneous.

It is clear that if we determine the simultaneity on a twisting body, the earth for example, the simultaneous instants being the mean times of passage of light or Hertzian signals, two given instants may be considered as simultaneous if we make the determination along a path which makes a sufficient number of complete turns round the earth. As a matter of fact, two events which occur at the same place on the equator with a difference of proper time of  $2 \times 10^{-7}$  sec. are simultaneous along the equator. A. A. Michelson \* has suggested a possible test of the rotation of the earth by interferential measures of simultaneity on the perimeter of a polygon, and experiments of this kind have been realized by G. Sagnac †, who succeeded in detecting the rotation of a twisting body by internal measures effected on it.

In these movements we use a parametric representation of the moving points, and the parameter  $t$  has no direct meaning of time.

Herglotz ‡ has shown that the movements of class B are one-parameter groups of movements in the universe, and he has determined from the theory of groups the four possible types of these movements.

#### I. Rotation of constant speed (elliptic group of Herglotz).

The equations of the movement are ( $\lambda$  constant):

$$\begin{aligned}\xi &= x \cos \lambda t - y \sin \lambda t, \\ \eta &= x \sin \lambda t + y \cos \lambda t, \\ \zeta &= z, \\ \tau &= t.\end{aligned}$$

\* Phil. Mag. viii. p. 716 (1904).

† C. R. clvii. pp. 708 & 1410 (1913).

‡ Loc. cit.

The corresponding interval may be written, using cylindrical coordinates :

$$ds^2 = -dr^2 - r^2 d\theta^2 - dz^2 - 2\lambda r^2 d\theta dt + (1 - \lambda^2 r^2) dt^2. \quad (33)$$

The lines of simultaneity of direction conjugate to  $dr = d\theta = dz = 0$  with respect to the light-cone are

$$-\lambda r^2 d\theta + (1 - \lambda^2 r^2) dt = 0,$$

and the spatial distance obtained by elimination of  $dt$  is

$$d\sigma^2 = dr^2 + \frac{r^2 d\theta^2}{1 - \lambda^2 r^2} + dz^2. \quad . \quad . \quad . \quad (34)$$

When  $r$  is a given function of  $\theta$  the lines of simultaneity are

$$t - t_0 = \lambda \int_{\theta_0}^{\theta} \frac{r^2 d\theta}{1 - \lambda^2 r^2}.$$

In the case of the earth, for  $\theta - \theta_0 = 2\pi$ ,  $\lambda = \frac{2\pi}{T}$ ,

$$t - t_0 \cong \frac{(2\pi r)^2}{T} = \frac{(2\pi r)^2}{T_{\text{sec.}} c^2} = \left(\frac{40}{300}\right)^2 \times \frac{1}{24 \times 60 \times 60} \\ = 2.06 \times 10^{-7} \text{ sec.}$$

## II. Hyperbolic group.

$$\xi = x + \lambda t,$$

$$\eta = y,$$

$$\zeta = z \cosh t,$$

$$\tau = z \sinh t.$$

The interval is

$$ds^2 = -dx^2 - dy^2 - dz^2 - 2\lambda dx dt + (z^2 - \lambda^2) dt^2. \quad (35)$$

For  $\lambda = 0$ , we obtain the hyperbolic movement which is the only one which belongs to both classes A and B.

The lines of simultaneity are

$$-\lambda dx + (z^2 - \lambda^2) dt = 0,$$

and the spatial distance

$$d\sigma^2 = \frac{z^2 dx^2}{z^2 - \lambda^2} + dy^2 + dz^2. \quad . \quad . \quad . \quad (36)$$

III. The third group (loxodromic group) is a combination of a rotation and an hyperbolic movement along the axis.

$$\begin{aligned}\xi &= x \cos \lambda t - y \sin \lambda t, \\ \eta &= x \sin \lambda t + y \cos \lambda t, \\ \zeta &= z \cosh t, \\ \tau &= z \sinh t.\end{aligned}$$

The interval is

$$ds^2 = -dr^2 - r^2 d\theta^2 - dz^2 - 2\lambda r^2 d\theta dt + (z^2 - \lambda^2 r^2) dt^2. \quad (37)$$

The lines of simultaneity are

$$-\lambda r^2 d\theta + (z^2 - \lambda^2 r^2) dt = 0,$$

and the spatial distance

$$d\sigma^2 = dr^2 + \frac{r^2 z^2 d\theta^2}{z^2 - \lambda^2 r^2} + dz^2. \quad . \quad . \quad . \quad (38)$$

IV. The last group (parabolic group) depends on two constants,  $\lambda$ ,  $\mu$ .

$$\begin{aligned}\xi &= x + \frac{1}{2}\lambda t^2, \\ \eta &= y + \mu t, \\ \zeta &= z + xt + \frac{1}{6}\lambda t^3, \\ \tau &= \lambda t + r + xt + \frac{1}{6}\lambda t^3.\end{aligned}$$

The interval is

$$ds^2 = -dx^2 - dy^2 - 2\mu dy dt + 2\lambda dz dt + (2\lambda x + \lambda^2 - \mu^2) dt^2, \quad (39)$$

and can be reduced, writing

$$x + \frac{1}{2\lambda}(\mu^2 - \lambda^2), \quad y, \quad \frac{1}{\sqrt{2\lambda}}(\mu y - \lambda z), \quad \frac{1}{\sqrt{2\lambda}}t$$

in place of

$$x, \quad y, \quad z, \quad t,$$

to the form

$$ds^2 = -dx^2 - dy^2 - 2dz dt + x dt^2. \quad . \quad . \quad . \quad (39')$$

The lines of simultaneity are

$$-dz + x dt = 0,$$

and the spatial distance

$$d\sigma^2 = dx^2 + dy^2 + \frac{dz^2}{x}. \quad . \quad . \quad . \quad (40)$$

It may be interesting to calculate the spatial curvature corresponding to these four types of movements.

For

$$d\sigma^2 = dx^2 + dy^2 + \phi^2 dz^2$$

the curvature is

$$R = \frac{2}{\phi} \left( \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right) \dots \dots \dots (41)$$

This formula may be applied to each of the four groups, and gives

$$\left. \begin{aligned} R_1 &= 6\lambda^2(1-\lambda^2 r^2)^{-2}, \\ R_2 &= 6\lambda^2(z^2-\lambda^2)^{-2}, \\ R_3 &= 6\lambda^2(r^2+z^2)(z^2-\lambda^2 r^2)^{-2}, \\ R_4 &= \frac{3}{2}x^{-2}. \end{aligned} \right\} \dots \dots (42)$$

$x$  and  $z$  are distances from a plane and  $r$  distance from a straight line. For  $R_3$  this axis is perpendicular to the plane.

Writing  $z = \lambda + x$  we find

$$R_2 = \frac{3}{2}x^{-2} \left( 1 + \frac{1}{2\lambda} x \right)^{-2},$$

which tends to  $R_4$  when  $\lambda$  tends to infinity.

In the motions of class A the geometry was Euclidean, *i.e.* of vanishing curvature, and the space might be considered as a plane section,  $t = \text{const.}$ , of the four-dimensional universe.

But in the motions of class B there is no time of simultaneity and the space cannot be considered as a section of the Galilean universe. Moreover, the element of length along every line of simultaneity is expressed by the root of a differential quadric which defines a Riemann geometry of the above curvatures (42).

These curvatures of space are the only possible ones which can be produced by movement of the solid of reference in a Galilean field.

Cambridge,  
March 6, 1924.

XX. *Adsorption from the Gas Phase at a Liquid-Gas Interface.*—Part II. By THOMAS IREDALE \*.

IN a previous communication (Phil. Mag. xlv. p. 1088 (1923)) the author described a method of measuring the surface tension of a liquid in contact with a vapour phase of varying composition, and studied in particular the change in the surface tension of mercury brought about by the adsorption of vapours of certain organic liquids. It was shown that, with a knowledge of the partial pressures of the vapours, and the use of the Gibbs adsorption equation, the excess of adsorbed vapour at the mercury surface could be calculated. It was thought remarkable that so few measurements of this interesting form of adsorption had ever been recorded in the literature of the subject; but it is noteworthy that as far back as 1877 Gibbs, in his original Memoir on Heterogeneous Equilibrium, suggested the possibility of calculating the amount of adsorption of water on mercury by noting the changes in the surface tension of the mercury under increasing partial pressures of water vapour.

*Adsorption and Condensation.*

In his original experiments the author generated vapours of different partial pressures by passing a slow current of dry air through organic liquids at different temperatures, and these air-vapour mixtures were then passed into a chamber at a somewhat higher temperature, where measurements of the surface tension of mercury were made. With methyl acetate vapour it was found that the surface tension fell rapidly with small partial pressures, but afterwards, as the pressure was increased, much more slowly, and became almost constant up to the point where the pressure was that of the saturated vapour. The curve indicating these changes was very similar to those usually obtained from data on the lowering of the surface tension of water by dissolving in it various "surface active" substances. It would seem in all these cases that the surface energy of the liquid ceases to change when the surface is saturated at a certain pressure or concentration with the molecules of the adsorbed substance. It was remarkable to observe, therefore, that when the vapour of the methyl acetate was saturated, great irregularities in the drop weight became apparent, the weight sometimes corresponding to what one would anticipate from the shape of the curve, namely, a surface tension of about

\* Communicated by Prof. F. G. Donnan, F.R.S.

415 dynes per cm., and sometimes to as low a value as 365 dynes per cm., though intermediate values were also obtained. As the calculations of the surface tension were always based on the average weight of a number of drops, such intermediate values might reasonably have been thought to be the means of several extreme values, presupposing a fluctuation of conditions during any single determination. By experimenting with single drops however, these intermediate values were found to have a real significance, and some of the results obtained in this way are recorded in Table I.

TABLE I.

Weight of drop of mercury formed in saturated methyl acetate vapour at 26° C.	Surface tension.
0.1471 gram.	
0.1620 ..	
0.1443 ..	
0.1598 ..	413 to 365
0.1628 ..	dynes per cm.
0.1533 ..	
0.1644 ..	
0.1454 ..	
0.1450 ..	

One would be inclined to think that this was due to varying degrees of condensation of liquid methyl acetate on the mercury surface, but the precise conditions controlling this degree of condensation were still open to question. There seemed to be no exact relationship between the rate of drop formation—always greater than three minutes—and the rate of condensation. At the same time irregularities were almost certain to creep into the results, owing to the way in which the saturated vapour was employed. The reader is referred to the original paper for experimental details; but it may be remarked that when the temperature of the saturators was maintained at 26° C., that is, above room temperature, it became necessary to slightly warm the tube passing from the saturators to the thermostat containing the drop-weight apparatus, in order to prevent condensation of the vapour in this tube. This tended to make the saturators work irregularly, and the current of vapour was not always continuous. An improvement was effected by discarding the original saturators, and using a series of the ordinary bubbling type, and the temperature being raised slightly

above  $26^{\circ}\text{C}$ ., the vapour began to condense on the walls of the glass dropping-chamber in the thermostat. The tendency of the vapour to condense on the mercury drop issuing from the pipette depended, of course, on the temperature fluctuation of its surface, and although the temperature fluctuation of the thermostat was never greater than  $0^{\circ}\cdot 2$  C., and might be much less than this in the case of the mercury enclosed in the glass chamber, one could never be sure how irregular the temperature of the vapour might be after passing through the heated connecting tube. This effect, of course, would seem to be very slight, but it is possible that the rate of condensation of a saturated vapour is influenced very greatly by small changes of temperature and pressure, and the adjustment to uniform conditions in the thermostat might be slower than anticipated, even with very slowly moving currents. The author was therefore led by these considerations to discard such a method of producing a saturated vapour, and to study the condensation process under more static conditions. It seemed reasonable, also, to abandon the use of such a substance as methyl acetate, which has some objectionable characteristics. It was found extremely difficult to remove the last traces of its vapour from the dropping-chamber, as it is apparently hydrolysed after a time, with the formation of acetic acid, on the walls of the chamber. Dry air was passed continuously through, but the mercury surface was still contaminated with traces of the acetate or acetic acid, the surface tension never rising higher than 450 dynes per cm. Treatment with ammonia vapour was found to be useless, and the whole apparatus was then dismantled, thoroughly cleaned and dried, and re-mounted, after changing the lubrication of the taps, etc. Those parts of the apparatus requiring lubrication are, it must be admitted, one of its principal defects, unless a suitable lubricating agent be found. A preparation of dextrin dissolved in glycerin was originally used for this purpose, but certain samples of dextrin were found to be unsuitable, as they appeared to give off vapours quite appreciably influencing the surface tension of mercury. But the mercury surface was not found to be so sensitive to the presence of vacuum tap grease, nor to metaphosphoric acid, and the former of these materials was therefore used with water vapour, and the latter with organic vapours. In order to obtain the highest value for the surface tension in dry air, it was found necessary to do away with the lubrication altogether, and sometimes to pass the air through permanganate solution, soda lime, sulphuric acid, phosphoric



oxide, and cotton wool, before it entered the dropping-chamber; and some samples of phosphoric oxide were found unsuitable for this purpose, owing, presumably, to the formation of some volatile compound. All this serves to show how sensitive the mercury surface is to the most minute traces of impurities adsorbed from the gaseous phase.

*The Adsorption and Condensation of Water Vapour.*

The presence of water vapour in the dropping-chamber was not found to influence the surface tension to any considerable extent, and this is due to the fact that its partial pressure at room temperature, even when saturated, is never very high. Consequently, when some determinations were carried out at room temperature ( $20^{\circ}\text{C}.$ ) outside the thermostat and in a space open to the atmosphere of the room, the degree of humidity of the atmosphere had very little effect on the results.

But when the vapour was saturated it was found possible, as in the case of methyl acetate, to actually condense the water on to the mercury surface, under certain conditions. The surface tension then fell to a very low value, corresponding to that found for the mercury-water interface.

Table II. records some of these measurements undertaken at  $26^{\circ}\text{C}.$ , and it will be seen that, owing to the low pressures of water vapour used, the surface tension is still changing fairly rapidly with the pressure, but at higher pressures one would expect the  $\sigma$ - $p$  curve to take the same form as the methyl acetate curve.

TABLE II.

Temperature of saturators.	Vapour pressure of water.	Drop weight.	Surface tension.
—	0 mm.	0.1903 gram.	472 dynes per cm.
$13.7^{\circ}\text{C}.$	11.6 "	0.1857 "	461 " "
$20.0$ "	17.5 "	0.1821 "	454 " "
$26.9$ "	25.0 "	0.1793 "	447 " "
	(saturated)	to	to
		0.1447 "	368 " "

In the case of the unsaturated vapours, air was bubbled slowly through the saturators, and determinations of the surface tension were made not only when the air-vapour mixture was passing through the dropping chamber, but also when it was kept steady in the chamber, by closing the tap  $T_2$  (see previous paper for diagram of apparatus), the correction to be applied for thermal transpiration being negligible.

The time of drop formation was never less than three and a half minutes, and when it was increased to ten minutes there was no appreciable change in the weight of the drop, so that it seems reasonable to suppose that the adsorption of the vapour is complete in this time.

In the case of the saturated vapour, however, a different procedure was adopted. The cup G was filled with water, and the ground glass joints of this part lubricated with the same liquid. The level of the water in the cup could be brought as near as desired to the drop issuing from the pipette. The temperature of the thermostat was then raised somewhat above 26° C. for a time, and on cooling to the original temperature with the tap T<sub>1</sub> closed, a slight blur on the walls of the dropping-chamber indicated condensation from a completely saturated vapour. As the walls of the chamber tended to cool faster than the pipette inside, condensation was more likely to occur on the walls than on the pipette, which was an advantage for the present purpose. As in the previous case of methyl acetate, variable results were obtained when the surface tension was measured in saturated water vapour (Table III.). But conditions were more under control than when the moving current of saturated vapour was used, and it was observed that the

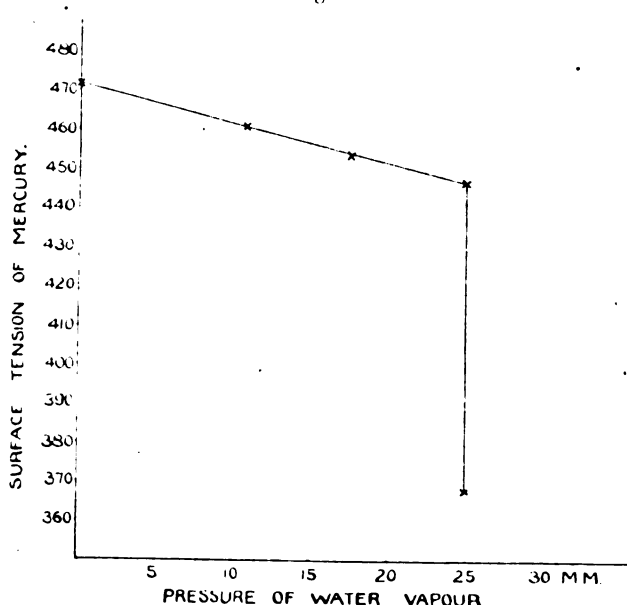
TABLE III.

Drop weights in grams, in saturated water vapour at 26° C.	Surface tension.
0.1515, 0.1642, 0.1574, 0.1770, 0.1632, 0.1792, 0.1448, 0.1603, 0.1704, 0.1782, 0.1770, 0.1665, 0.1477, 0.1767, 0.1742, 0.1754, 0.1682, 0.1724.	447 to 368 dynes per cm.

more slowly the drop was formed, and the nearer it was allowed to hang to the surface of the water in the cup, the smaller was its size, and the lower, therefore, the surface tension. The smallest values recorded in Table III. were obtained by allowing the drop to form about 1 mm. above the water surface, in a time varying from 3½ to 20 minutes. When the period fell below 3½ minutes, however (Table IV.), the drop weight increased very considerably, indicating a surface tension no less than that obtained by allowing the drop to form at a distance of over 1 cm. from the water

surface, which is what one would anticipate to be the surface tension in the saturated vapour from the curve (fig. 1) drawn with the aid of the data in Table II.

Fig. 1.



As a matter of fact, it was found almost impossible to condense the water on to the mercury surface if the drop were formed sufficiently distant from the water surface even if the period were as much as twenty minutes or more. These effects may be due, in part, to the variation in density of the vapour as we pass upwards from the water surface, but it is obvious that diffusion also plays a part in the phenomenon.

TABLE IV.

Period of drop.	Drop weight.	Surface tension.
3½ minutes to	0.1455 to	370 to
20 "	0.1448 gram.	368 dynes per cm.
2 "	{ 0.1799 } { 0.1793 } gram.	447 " "

The detachment of the drop had always to be very carefully watched, as certain irregularities were observed when any moisture condensed on the tip of the pipette, a

difficulty which could not always be obviated. The water sometimes tended to displace the mercury in the pipette, and when the drop broke off it was followed by a small secondary droplet, detached from the interior of the pipette just above the orifice. If the water formed a visible skin around the mercury, the drop was able to grow to a larger size than usual, owing to the additional support against gravity afforded by the skin. This is a rather important observation, as it shows that the invisible *condensed* film of water responsible for such a large decrease in the surface tension previously observed, must still be very thin compared with the dimensions of the drop itself. The surface tension measured in this case must really be the interfacial tension between the mercury and the water, and not the tension of the composite surface, mercury/water-water/air.

These results admit of a logical interpretation if we assume that there are two kinds of film in equilibrium with a liquid when another liquid tends to spread over its surface. The primary film, which may be only one or two molecules thick, is formed from the vapour of the spreading liquid. The secondary or condensed film, which is formed when the liquid has completely spread over the surface, may sometimes be much thicker than this, with corresponding differences in the interfacial tension. Some observations of Hardy (Proc. Roy. Soc. A, lxxxviii. p. 316 (1913)) lend support to these assumptions. He found that when a substance like benzene was spread over a water surface, lenses might be formed which were in equilibrium with a film of the benzene forming a composite surface with the water. This was possible because  $T_B > T_A + T_{AB}$ , where  $T_{AB}$  is the interfacial tension, and  $T_A$ ,  $T_B$ , the surface tensions of benzene and water respectively. But with certain saturated substances where  $T_B < T_A + T_{AB}$ , spreading of this kind could not occur, though the vapours of these substances were able to condense on the surface, since  $T_{AB} < T_B$ . A film formed in this way could not have the properties of the liquid *en masse*, and no composite surface could be formed. The first of these conditions would hold in the case of water spreading on mercury (Harkins and Feldman, Jour. Amer. Chem. Soc. xlv. p. 2681 (1922)), since in this case  $T_B > T_A + T_{AB}$ , but in the author's mode of experiment the formation of the primary film preceded that of the condensed film, which, owing to diffusion or some other unavoidable factor, took a somewhat longer time for its completion.

In the present experiments which deal with the adsorption of molecules from the vapour phase, it is possible that the

primary phenomenon is the gradual formation of a unimolecular layer. The initial surface tension-vapour pressure curve would then correspond to the formation and perhaps, also, the compression of such a unimolecular layer (compare the work of Langmuir and Adam on the formation of unimolecular layers of fatty acids and other substances on a water surface). It must be remarked, however, that if the molecular attractive forces fall off very rapidly with distance, the effect on the surface tension might be due primarily to the first layer of molecules, and thus possibly the Gibbs equation might indicate a unimolecular layer, though in reality there were present in adsorption equilibrium a layer several or many molecules thick. After the vapour reaches the saturation value for a plane surface at a given temperature, the experimental data indicate that a new regime sets in.

In this case a very thin film of liquid may condense on the mercury surface, the thickness of which is not a determinate function of the pressure and temperature, though the most stable state corresponds to the formation of a film, which may, from the standpoint of intermolecular forces, be regarded as infinitely thick. In this region (saturated vapour) the experimental data indicate a very abrupt fall in the interfacial tension, the lowest value corresponding to the interfacial tension between mercury and liquid water in bulk. The formation of such a film will probably result in a still closer packing of the layer of molecules adjacent to the mercury surface.

The author is not aware that any experiments have been carried out on the compression of films on a mercury surface, but Hardy (Proc. Roy. Soc. A, c. p. 550 (1922)) has obtained some interesting results on lubrication, where primary films formed from organic vapours on a bismuth or glass surface were subjected to tangential forces. With the saturated vapour it was possible to obtain the same value for the coefficient of static friction as with a layer of the liquid itself. But these results are not quite in harmony with the author's for the following reason. There was a gradual change in the friction as the vapour pressure approached the saturation value, whereas the surface tension was always found by the author to change abruptly in the saturated vapour in the several cases examined (water, methyl acetate, benzene, etc.), even when an adsorption maximum was indicated by the curve at pressures much below the saturation pressure. The molecules on the mercury surface were not, of course, subjected to any external forces while

the drop was forming, but the two phenomena differ also in some other respects. In the experiments on static friction the vapour pressure of the lubricant had to exceed a definite small value before any change in the friction could be observed. The surface tension of the mercury, on the other hand, is sensitive to the most minute traces of organic vapours, at vapour pressures presumably very much lower than this limiting value in the friction experiments. There possibly is a limiting pressure for the surface tension, but it is too small to be appreciable in the present experiments.

Another important factor is the time of formation of the primary film. Hardy found with some substances that the molecules took twenty minutes or more to orient themselves on the surface. The author has always observed, on the other hand, that the adsorption of *unsaturated* vapours on the mercury surface is a very rapid process, and the maximum lowering of the surface tension occurs in less than a minute. The somewhat longer time necessary to form the *condensed* film from the saturated vapour must depend more on the rate of diffusion of the molecules to the surface, and hence the presence of the air and the distance of the mercury drop from the water surface must be the principal factors in the process. To test these points further the author has begun some experiments on the adsorption of vapours in the absence of air, which will be discussed later.

A few words may be said here about the work of Cantor (Wied. Ann. lvi. p. 492 (1895)) which has a direct bearing on the present experiments. Cantor argued that it was possible to condense the vapour of a liquid on to the surface of another liquid at a pressure less than the saturation pressure, owing to the decrease in free energy at the surface. The particular equation he derived is true only in so far as the pressure is independent of the thickness of the condensed film; but he afterwards ignores this assumption in deriving the equation for the tension of the composite surface. The argument is faulty and is based on incomplete experimental evidence. From the author's results it would seem that the transition from an adsorbed film, possibly only one molecule in thickness, to a condensed film having the properties of the liquid in bulk, is more abrupt than was to be anticipated on any such theory as Cantor's.

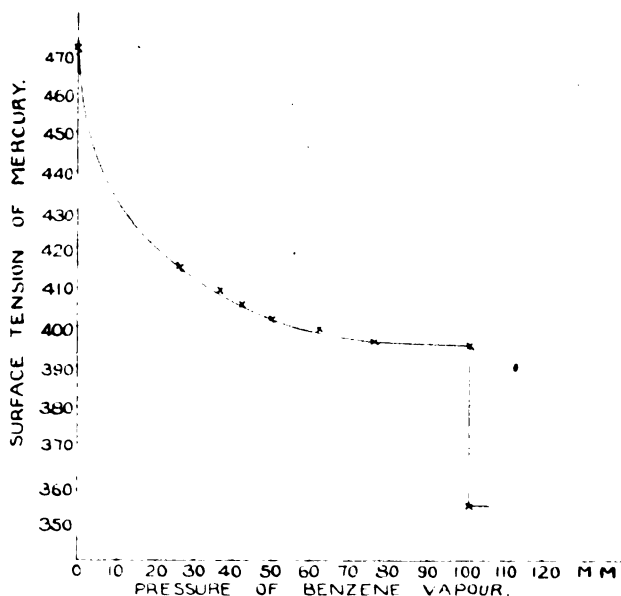
Cantor considered that, because the vapours of benzene and amyl alcohol generated at  $21^{\circ}\text{C}$ . were able to lower the surface tension of mercury at  $23^{\circ}\text{C}$ ., there were good grounds for supposing that condensation of the vapours had occurred at a temperature above the saturation temperature,

and consequently below the saturation pressure. These results do not necessarily indicate that condensation has occurred, and so far as the author can see from the actual values of the surface tension change, they merely show the existence of a primary "gaseous" film.

*The Adsorption and Condensation of Benzene Vapour.*

Of the other substances studied the most interesting was benzene. A pure specimen of this liquid was obtained by freezing a good thiophene-free sample that had been used for cryoscopic purposes. The crystals were melted and the liquid distilled, the portion boiling at  $80^{\circ}\text{C}$ . being collected. It was afterwards dried over phosphoric oxide and again distilled.

Fig. 2.



The results of experiments with benzene vapour are recorded in Table V., and the curve in fig. 2 was constructed with the aid of these data. It is similar in form to the previous curve obtained with methyl acetate, and illustrates an apparent adsorption maximum before condensation of the vapour takes place.

The results in Table VI. show that, as in the case of water vapour, the condensation of benzene under static conditions takes some minutes for its completion.

*The Reversibility of the Phenomenon.*

When the drop issuing from the pipette had grown to a certain size in the vapours of water or benzene, and was about to break off, this detachment could sometimes be retarded by dexterously forcing a current of dry air into the dropping-chamber, and sweeping out the vapour. The fact that the drop could afterwards grow to a larger size before detaching is some evidence for the belief that the phenomenon is a reversible one, as the surface tension was evidently increased by desorption of the vapour.

TABLE V.

Temperature of saturators.	Vapour pressure of benzene.	Drop weight.	Surface tension.
—	0 mm.	0.1903 gram.	472 dynes per cm.
0° C.	26.5 "	0.1668 "	415 " "
5.4 "	37.0 "	0.1636 "	410 " "
8.1 "	42.1 "	0.1610 "	406 " "
11.2 "	49.9 "	0.1592 "	402 " "
15.5 "	61.8 "	0.1583 "	400 " "
20.0 "	76.3 "	0.1565 "	396 " "
26.0 "	101.0 "	0.1562 "	395 " "
	(saturated vapour).	to 0.1416 "	354 " "

TABLE VI.

Condensation of benzene on mercury near the benzene surface.

Period of drop.	Drop weight.	Surface tension.
2 minutes	0.1522 grams.	388 dynes per cm.
5—20 "	0.1416 "	354 " "

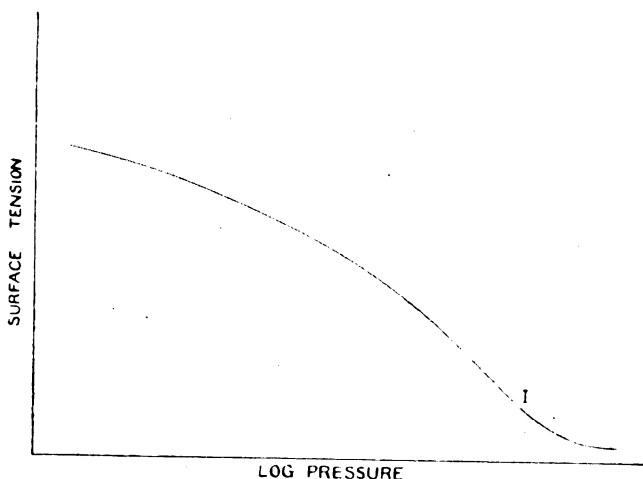
*The Calculation of  $\Gamma$  from the  $\sigma$ - $p$  Curve.*

The tangent to the  $\sigma$ - $p$  curve, the value of  $\frac{d\sigma}{dp}$ , enters into the Gibbs equation for calculating the value of  $\Gamma$ , the excess surface concentration of vapour. Such a calculation is meaningless, however, when the curve becomes asymptotic to the line of lowest surface tension, as the tangent gradually approaches a zero value. All we are concerned with is the maximum value of  $\Gamma$ , and that such a maximum exists is evident from the following considerations.



The Gibbs equation,  $\Gamma = -\rho \frac{d\sigma}{dp}$ , since  $\rho$  is proportional to  $p$ , may be written in the form  $\Gamma = -k \frac{d\sigma}{d \log p}$ , where  $k$  is a constant. Taking the values of  $\log p$  for the abscissæ, and those of  $\sigma$  for the ordinates, the usual form of curve would be as shown in fig. 3. The value of  $\frac{d\sigma}{d \log p}$  passes

Fig. 3.



through a maximum at the point of inflexion I, and so also must the value of  $\Gamma$  be a maximum at this point. The theory, of course, is quite unable to predict the shape of the curve, but in making any calculation of  $\Gamma$ , especially when we desire to know the actual value of the saturated adsorption, it is important to bear this point in mind, though most investigators seem hitherto to have ignored it.

In the case of water vapour at the pressures examined, the curve (fig. 1) does not indicate a maximum value of the surface adsorption, which is still changing fairly rapidly with the pressure, just before the saturation point.

The value of  $\Gamma$  at the saturation point was found to be  $1.8 \times 10^{-8}$  gram per sq. cm., which is somewhat less than that required for a monomolecular film ( $3 \times 10^{-8}$ ; see also Langmuir, Jour. Amer. Chem. Soc. xl. p. 1379 (1918)).

The maximum value of  $\Gamma$  for benzene was found to be  $6.2 \times 10^{-8}$  gram per sq. cm. From this it can be calculated that the area per molecule on the surface is  $21 \times 10^{-16}$  sq. cm. This is very near the value  $23.8 \times 10^{-16}$  sq. cm. which

Adam (Proc. Roy. Soc. A, *ciii*. p. 676 (1923)) gives for the area per molecule of certain benzene derivatives on the surface of water.

There seems to be some evidence, therefore, for the assumption that vapours adsorbed on the surface of mercury tend to form primary monomolecular films.

### *The Surface Tension of Mercury in a Vacuum.*

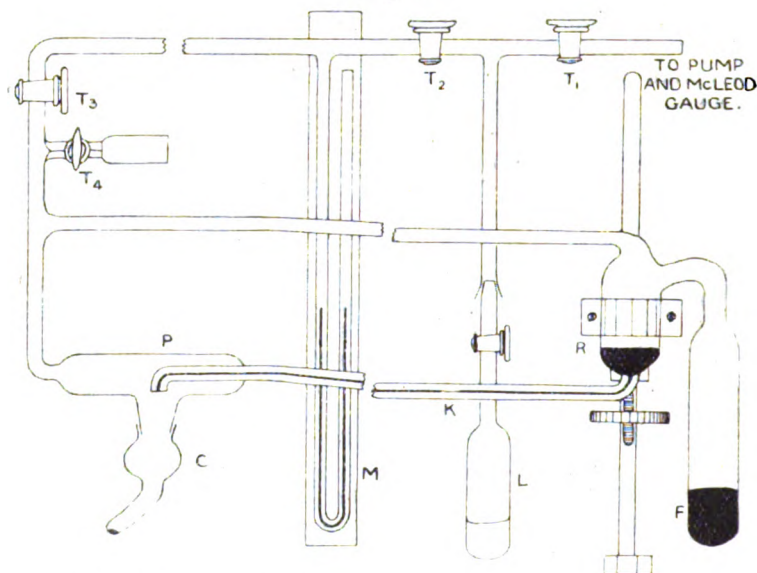
There exist some discrepancies in the literature dealing with the measurement of the surface tension of mercury in a vacuum. The results of Stockle (Wied. *Ann.* *lxvi*. p. 499 (1898)), which are more often quoted than any others, show some remarkable anomalies. He found that the surface tension in air and certain gases was always higher than in a vacuum, but it fell after a time to the same value. More recent experiments, those of Hogness (Jour. Amer. Chem. Soc. *xliii*. p. 1621 (1921)), Harkins and Ewing (*ibid.* *xlii*. p. 2539 (1920)), Palacios and Tasala (*Anal. Fis. Quim.* *xx*. p. 505 (1922)), do not confirm these results, and these workers found that the surface tension was either the same in a vacuum as in dry air and other indifferent gases, or, if anything, a little higher. One would expect the adsorption of gases to lower the surface tension, and would be inclined to think that these later experiments were more reliable, though Stockle's experiments seemed to be carried out with no less care and precaution. It was obvious to the author that this point must be finally settled before continuing investigations on the adsorption of vapours.

Devices for measuring the surface tension of mercury in a vacuum by the drop-weight method have been described by Cenac (*Ann. de Chim. Phys.* *xxix*. ser. 8, p. 298 (1913)) and Harkins and Ewing (*loc. cit.*), but they were not found wholly suitable for the present purpose. In addition to this type of measurement, the surface tension in vapours unmixed with air had to be measured at different pressures and temperatures, and the device had also to allow of a varying period of drop formation—a few seconds to an hour or more,—which considerably increased the difficulties of the technique.

The original apparatus went through several stages in its development, but the final form adopted will be readily understood from the diagram (fig. 4). The distance between the dropping-chamber P and the container R was about four feet, giving considerable flexibility to the device, and permitting the container to be raised and lowered through a

distance of several centimetres. The level of the mercury in the container was always higher than the column of mercury throughout the length of the capillary tube, so that no part of the column was under a negative pressure when the apparatus was evacuated. The minute capillary K was introduced some distance down the tube, so as to be on the same level as the orifice. These precautions were taken to minimize the danger of the column detaching at any point, as great difficulty was experienced in getting regular drop formation in some of the earlier apparatus, owing to defects

Fig. 4.



of this kind. The tip of the pipette was made in the manner described in the previous paper, and the diameter measured with the aid of a travelling microscope. It was necessary for the orifice to be only one centimetre from the bend in the tube, and some of the tubes had to be discarded on this account, as the bending tended to make the capillary elliptical in cross-section.

The apparatus was evacuated by means of a two-stage mercury vapour pump, operated by a Toepler pump. This arrangement helped to promote a quiet and regular ebullition of the mercury in the vapour pump, and hence to minimize vibration effects.

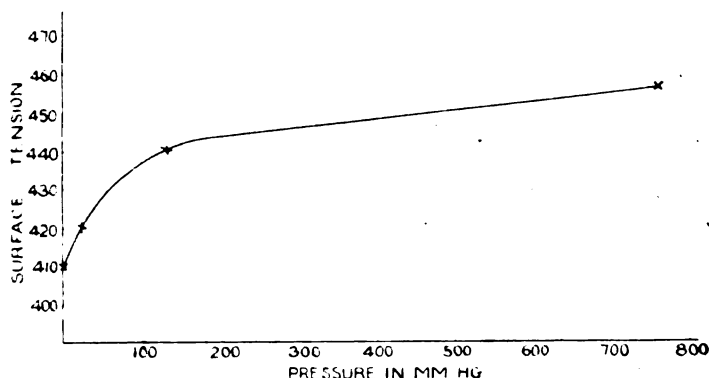
In the first experiments pure mercury was transferred to F, and distilled over into R at a pressure of  $10^{-5}$  mm. In removing the cup C, air from the room passed into the apparatus, in addition to air already admitted by the tap T, and then some rather remarkable results were obtained.

TABLE VII.

Temperature 18-19° C.		Surface tension.	
In air, pressure 763 mm.		456 dynes per cm.	
..	130 ..	440	.. ..
..	24 ..	420	.. ..
..	$10^{-4}$ ..	410	.. ..

As the pressure of the air in the apparatus was decreased, the surface tension gradually fell, and diminished very rapidly as the pressure became very low (Table VII. and fig. 5). It seemed as though it were a selective adsorption

Fig. 5.



effect, some impurity tending to adsorb on the mercury surface more readily in a vacuum than in air. Such an impurity would obviously be of a condensable kind, not readily detectable by the McLeod gauge, and might be water vapour—always the last gas to be removed from any vessel,—or some volatile compound from the lubricant of the taps, or from the phosphoric oxide used for drying purposes. The effects were apparent, however, whether the phosphoric oxide tube were inserted or not, and a change of lubricant from rubber grease to meta-phosphoric acid did not alter the results. Attempts were made to do away with the lubricant altogether and to use mercury seals, the manometer M and the flask L were removed, and a liquid-air trap inserted

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between the mercury-vapour pump and the dropping-chamber. These changes, however, were without effect, and it would seem that the impurity was coming from the glass or from the mercury itself. The apparatus was then dismantled and thoroughly re-cleaned, and dried in a current of hot air. The mercury was re-distilled, twice in a current of air, and then *in vacuo*. Determinations were then made as quickly as possible after distilling the mercury into the container. The surface tension was found under these conditions to be 475 dynes per cm. at a pressure of  $10^{-5}$  mm. On admitting air it fell to about 460, and on re-evacuating to  $10^{-5}$  mm. it decreased, as before, to 410 dynes per cm.

TABLE VIII.

		Period of drop.	Surface tension.	
In air, atmospheric pressure				
760-750 mm.		30 seconds.	456	dynes per cm.
		5-10 minutes.	450-448	„ „
		1-2 hours.	450-446	„ „
pressure	13 mm.	10 seconds.	460	„ „
		1 minute.	440	„ „
		5-10 minutes.	427	„ „
pressure	$10^{-4}$ mm.	20 seconds.	417	„ „
		5-10 minutes.	412	„ „

It was interesting to observe also that the impurity was adsorbed more quickly in a vacuum than in air (Table VIII.).

Hogness (*loc. cit.*) states that a thorough preliminary heating of his apparatus was necessary in order to obtain the maximum value for the surface tension. This was presumably to drive out all the condensed water from the system, which the vacuum pump, of itself, was unable to do. Harkins and Ewing (*loc. cit.*) merely state that the pressure in their vacuum was so low as to be undetectable by the McLeod gauge (below  $10^{-7}$  mm.). These workers did not observe the interesting phenomenon described in this paper, but they seem to have adjusted conditions whereby it would be overlooked.

On admitting water vapour into the dropping-chamber—temperature  $18^{\circ}$  C. and pressure 15.5 mm.—the surface tension was found to be 411 dynes per cm. The vapour was saturated, but did not readily condense on the mercury surface. This is much the same as the surface tension *in vacuo*, and it is possible that the adsorption of water vapour

from the glass of the apparatus is responsible for the anomalies that have been observed.

It is possible, also, that the presence of air may raise the pressure of water vapour necessary to form a saturated, adsorbed film, but this by no means invalidates any of the conclusions arrived at in the earlier part of this paper. At the same time, it seems remarkable that an adsorbed film of water at ordinary temperatures can exist on a mercury surface at so low a pressure as  $10^{-5}$  mm. This matter is being further investigated, but it would seem that similar effects to those described were operative in Stockle's experiments, and were responsible for the anomalies he observed.

I am indebted to Professor Donnan for the great interest he has taken in this investigation, and to the Royal Commissioners of the 1851 Exhibition for a scholarship which is enabling me to continue the work.

The William Ramsay Laboratories of  
Inorganic and Physical Chemistry,  
University College, London,  
April 23, 1924.

ERRATA.

Phil. Mag. xlv. 1:23:—

Page 1090, lines 13, 14, read: "any liquid of known density."

Page 1093, line 8, read: "density of benzene at this temperature is 0.879."

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XXI. *Adsorption Forces and their Electrical Nature.* By  
Professor BORIS ILIIN, the Physical Institution of the  
Science Institution of Moscow\*.

[A Preliminary Report.]

THE existence of a close relation between adsorption and the phenomena of surface tension, the phenomena of the potentials of electrodes, the phenomena of electrocapillarity, the coagulation of colloidal solutions under the influence of electrolytes, leads to the problem of the electrical nature of the forces of adsorption. But if one considers the potential of adsorption as electric, one is able to look for definite relations between electrical constants and the adsorption capacity  $C_{\infty}$  and the heat of adsorption  $Q$ , because the relation of  $C_{\infty}$  and  $Q$  to the adsorption potential

\* Communicated by the Author.

Phil. Mag. Ser. 6. Vol. 48. No. 283. July 1924.

can be established by aid of the reasonings of Eucken \* which led him to the formula :

$$C_{\infty} = \frac{S\sigma\eta_0 e^T}{\mu \frac{c}{T}}$$

Here S is the surface of adsorption.

$\sigma = \rho_1 + \rho_2$ , where  $\rho_1$  and  $\rho_2$  are the radii of the molecules of the adsorbent and the adsorbed substance respectively.

$C = \frac{a}{\sigma^\mu R} = -\frac{K_\sigma}{R}$ , whereas  $K_\sigma$  is a private quantity for the potential of attraction  $K = \frac{a}{r^\mu}$  for  $r = \sigma$ .

Using the same method †, and considering the potential of attraction as an electric potential, I arrived at the relation :

$$C_{\infty} = S\eta_0 \frac{RT r_0^\nu}{b} \left[ e^{\frac{b}{RT r_0^\nu} (r_0 - \sigma)} - 1 \right], \quad . \quad . \quad (1)$$

where  $r_0$  is the width of the adsorption film, and "b" enters into the expression for the force of adsorptive attraction  $F = \frac{b}{r^\nu}$  and is defined by the position of electrical charges of electrical fields of the adsorbent and of the adsorbed substance ‡.

For the case of the adsorption of ions

$$b = b' \kappa \eta,$$

where  $\eta$  is the elemental electric charge,  $\kappa$  the valency of the ions,  $b'$  a constant.

Therefore

$$C_{\infty} = S\eta_0 \frac{RT r_0^\nu}{b' \kappa \eta} \left[ e^{\frac{b' \kappa \eta}{RT r_0^\nu} (r_0 - \sigma)} - 1 \right], \quad . \quad . \quad . \quad (2)$$

a relation which gives an explanation of the strong augmentation of the coagulating action with addition of electrolytes of higher valency ‡.

\* Eucken, *Ber. d. deutsch. Phys. Ges.* xvi. p. 345 (1914).

† For a more general case, when adsorption is not limited by the surface densification alone, I developed a general theory of adsorption processes, tested by experiments. *Vide* Iliin, 'Reports of the Physical Institution of the Science Institution of Moscow,' i. (1921); Iliin, *Zeit. f. phys. Chem.* cvii. p. 145 (1923).

‡ Iliin, 'The Electrical Nature of the Adsorption Forces': a Report to the Physical Institution of the Moscow Sci. Inst. Dec. 1920; "On the Theory of Absorption Processes," Proceedings of the 3rd Mendeleejev Congress at Petrograd, May 1922.

The aim of this work is, besides the equations (1) and (2), to find even definite relations between the adsorptive constants  $C_\infty$  and  $Q$  and the dielectric constant  $\epsilon$  of the adsorbed gas—considering not the *adsorption of ions* but the adsorption of neutral molecules, and considering the neutral molecule as a compound of positive and negative charges according to contemporary conceptions of electron-theory displaced under the influence of the external electrical field of the adsorbent.

In fact, if the forces of adsorption are of electro-statical origin, then the tension of the field of the adsorbent  $E$  placed in an adsorbed gas is defined by a known relation :

$$E = E_0 - 4\pi N d\eta',$$

where  $d\eta'$  is defined by a displacement of charges in the gas molecule under the influence of the field;  $d$  is the distance between the displaced charges,  $\eta'$  the size of the charge,  $N$  the number of the charges of both signs in a unit of volume;  $E_0$  the tension of the field of adsorption in a vacuum;  $E = \frac{E_0}{\epsilon}$  the tension of the field of adsorption in a gas with a dielectric constant  $\epsilon$ .

Therefore

$$\tau = d \cdot \eta' = \frac{E_0}{4\pi N} \left( \frac{\epsilon - 1}{\epsilon} \right). \quad . \quad . \quad . \quad (3)$$

For the tension of a field of adsorption, leaving the question of the distribution of the electric charges on the adsorbent open, we make use of the expression

$$E_0 = \frac{e_1}{r^\nu},$$

where  $e_1$  characterizes the electric density on the adsorbent. For the force of the field of adsorption acting on the neutral molecule, we have

$$F = e_1 \cdot \eta' \left( \frac{1}{r^\nu} - \frac{1}{(r+d)^\nu} \right) = e_1 \cdot \eta' \frac{\nu \cdot d}{r^{\nu+1}},$$

and considering (3),

$$F = e_1 \cdot \nu \frac{\tau}{r^{\nu+1}} = \frac{e_1 \nu}{r^{\nu+1}} \frac{E_0}{4\pi N} \left( \frac{\epsilon - 1}{\epsilon} \right) \quad . \quad . \quad . \quad (3')$$

for the given case "b" in the formula (1) is equal to

$$e_1 \cdot \nu \frac{E_0}{4\pi N} \left( \frac{\epsilon - 1}{\epsilon} \right) \cdot r^{-1},$$



and substituting this expression in the formula (1), we obtain

$$C_{\infty} = S \cdot \eta_0 \frac{RT r_0^{\nu+1}}{e_1^{\nu} \frac{E_0}{4\pi N} \left( \frac{\epsilon-1}{\epsilon} \right)} \left[ e^{\frac{e_1^{\nu} \frac{E_0}{4\pi N} \left( \frac{\epsilon-1}{\epsilon} \right)}{RT r_0^{\nu+1}} (r_0 - \sigma)} - 1 \right], \quad (4)$$

or in rejecting the unity in comparison with

$$e^{\frac{e_1^{\nu} \frac{E_0}{4\pi N} \left( \frac{\epsilon-1}{\epsilon} \right)}{RT r_0^{\nu+1}} (r_0 - \sigma)},$$

we have

$$\log \left\{ C_{\infty} \cdot \left( \frac{\epsilon-1}{\epsilon} \right) \right\} = \log A + B \left( \frac{\epsilon-1}{\epsilon} \right) \log \epsilon,$$

where A and B are expressions no longer containing the dielectric constant  $\epsilon$ . The following Table I. (Graph 1) gives corresponding experimental data:—

TABLE I. (Graph 1.)

Dielectric Constant  $\epsilon$  and the Adsorption Capacity  $C_{\infty}$ .

Adsorbed gas.	Dielect. constant $\epsilon$ .	$\log C_{\infty}$ .		$\log \left\{ C_{\infty} \left( \frac{\epsilon-1}{\epsilon} \right) \right\}$ .	
		Data of I. H. Homfray.	Data of A. Titoff.	Data of I. H. Homfray.	Data of A. Titoff.
H <sub>2</sub> .....	1.000264	.....	-0.644	.....	-4.224
Ar .....	557	-1.11+3	.....	-1.36	.....
N <sub>2</sub> .....	581	-0.92+3	+0.37	-1.16	-2.87
CO .....	695	-0.70+3	.....	-0.86	.....
CH <sub>4</sub> .....	944	-0.25+3	.....	-0.27	.....
CO <sub>2</sub> .....	985	+0.20+3	+1.48	+0.19	-1.53
C <sub>2</sub> H <sub>4</sub> .....	1312	+0.58+3	.....	+0.70	.....

The linear interrelation between  $\log \left\{ C_{\infty} \left( \frac{\epsilon-1}{\epsilon} \right) \right\}$  and  $\frac{\epsilon-1}{\epsilon}$  required according to the theory is confirmed.

Because the heat of adsorption Q is defined by the potential of attraction, it is evident that according to the

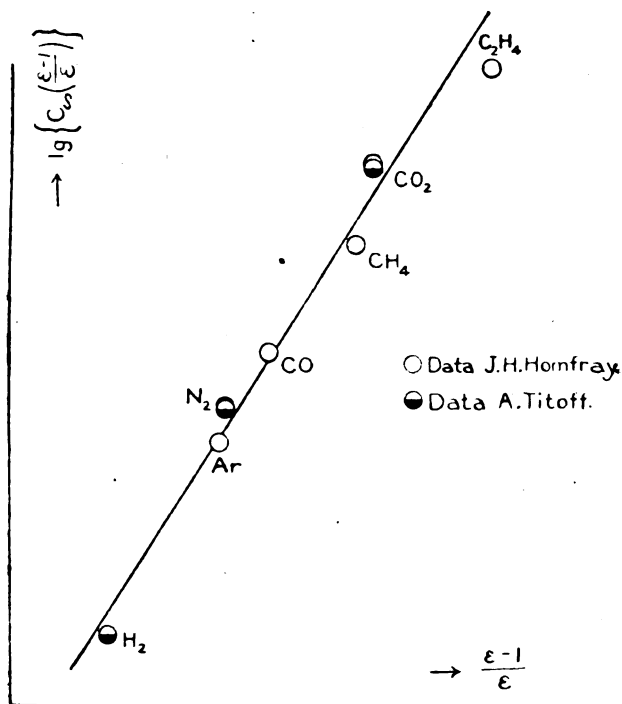
above-mentioned considerations a definite relation must exist between  $Q$  and  $\epsilon^*$ .

In a vacuum the adsorbent (also cool) has an external energy of a field of adsorption whose density is expressed by

$$W_0 = \frac{E_0^2}{8\pi},$$

where  $E_0$  is the tension of the field of adsorption in a vacuum.

Graph 1.



If the adsorbent is placed in a gas with a dielectric constant  $\epsilon$ , then the density of the energy of the field of adsorption has to change into

$$W_1 = \frac{\epsilon E^2}{8\pi},$$

where  $E = \frac{E_0}{\epsilon}$  is the tension of the field of adsorption in a given gas with a dielectric constant  $\epsilon$ .

\* The deduction and the calculations concerning  $Q$  were made by my co-worker, Mr. B. B. Tarasov, who is working with a great amount of material and whose work is shortly going to press.

The difference  $W_0 - W_1$  defines the specific heat of absorption  $Q$  :

$$Q = W_0 - W_1 = \frac{E_0^2}{8\pi} - \frac{\epsilon E^2}{8\pi} = \frac{E_0^2}{8\pi} \left( \frac{\epsilon - 1}{\epsilon} \right).$$

The same result can be obtained if one considers  $Q$  as a potential of the force of adsorbing attraction :

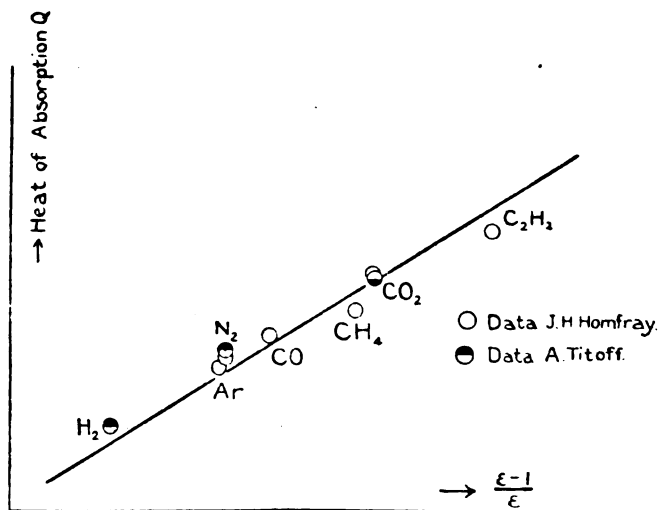
$$F = \frac{e_1 \cdot \nu}{r^{\nu+1}} \frac{E_0}{4\pi N} \left( \frac{\epsilon - 1}{\epsilon} \right).$$

TABLE II. (Graph 2.)

Dielectric Constant  $\epsilon$  and the Heat of Adsorption  $Q$ .

Adsorbed gas.	Dielectric constant $\epsilon$ .	The Heat of Adsorption, $Q$ .	
		Data of I. H. Homfray.	Data of A. Titoff.
H <sub>2</sub> .....	1.000264	.....	2408
Ar .....	557	3993	.....
N <sub>2</sub> .....	581	4270	4460
CO .....	695	4860	.....
CH <sub>4</sub> .....	944	5570	.....
CO <sub>2</sub> .....	985	6560	6467
C <sub>2</sub> H <sub>4</sub> .....	1312	7800	.....

Graph 2.



Experimental data prove the proportionality between  $Q$  and  $\frac{\epsilon - 1}{\epsilon}$  as required by the theory quite satisfactorily,

especially if one takes into consideration considerable mistakes in the definition of the heat of adsorption and of the dielectric constants.

As Debye \* has shown, the constant of attraction in the equation of van der Waals is nothing else but the electrostatic energy of the molecular attraction, or, according to our conceptions, a quantity related to  $\frac{\epsilon-1}{\epsilon}$ . Without establishing any definite law, we give here items which show a quite definite parallelism in the growth of  $\log C_{\infty}$ ,  $Q$ ,  $\frac{\epsilon-1}{\epsilon}$ , and of the constant of van der Waals.

TABLE III.

Attraction-Constant of van der Waals and Adsorption Constants.

Adsorbed gas.	Dielect. const. $\epsilon$ .	$\log C_{\infty}$		$Q$ .		Attraction-constant of van der Waals.
		Data of I. H. Homfray.	Data of A. Titoff.	Data of I. H. Homfray.	Data of A. Titoff.	
H <sub>2</sub> .....	1.000264	.....	-0.644	.....	2408	0.00042
Ar .....	557	-1.11+3	.....	3993	.....	259
N <sub>2</sub> .....	581	-0.92+3	+0.37	4270	4460	268
CO .....	695	-0.70+3	.....	4860	.....	275
CH <sub>4</sub> ...	944	-0.25+3	.....	5570	.....	367
CO <sub>2</sub> ...	985	+0.20+3	+1.48	6560	6467	699
C <sub>2</sub> H <sub>4</sub> ...	1312	+0.58+3	.....	7800	.....	833

### Conclusions.

The general results of this work are as follows :—

(1) On the basis of a conception of an electric nature of the forces of adsorption, we have obtained a relation between the adsorption capacity  $C_{\infty}$  and the dielectric constant of the adsorbed gas  $\epsilon$  in the form

$$C_{\infty} = S \cdot \eta_0 \frac{RT r_0^{v+1}}{e_1 \frac{E_0}{4\pi N} \left( \frac{\epsilon-1}{\epsilon} \right)} \left[ e^{\frac{e_1 v}{4\pi N} \frac{E_0}{r_0^{v+1}} \left( \frac{\epsilon-1}{\epsilon} \right) (r_0 - \sigma)} - 1 \right],$$

which is proved by experimental data.

(2) On the basis of the same conceptions, the heat of adsorption  $Q$  is defined by the difference between the external energy of the adsorption field of the adsorbent in a vacuum

\* Debye, *Phys. Zeit.* xxi. p. 178 (1920).

and in a given gas with a dielectric constant  $\epsilon$ , and for  $Q$  we have obtained the equation :

$$Q = \frac{E_0^2}{8\pi} \left( \frac{\epsilon - 1}{\epsilon} \right).$$

This relation is in good accordance with experimental data.

(3) A definite parallelism in the changes of  $\log C_\infty$ ,  $Q$ ,  $\frac{\epsilon - 1}{\epsilon}$ , and of the constant of van der Waals is established.

Finally I have to express my deep gratitude to the Member of the Russian Academy of Science, Professor P. P. Lasareff, the Director of the above-named Institution, where some of my work and that of my co-workers is conducted, for the lively interest and attention given by him to it.

Physical Institution of the  
Science Institution of Moscow,  
11th August, 1923.

## XXII. *The Number of Alpha-Particles emitted by Radium.*

By VICTOR F. HESS, *Ph.D.*, and ROBERT W. LAWSON, *D.Sc., F.Inst.P.\**

**I**N a recent communication (*Zeit. f. Physik*, vol. xxi. pp. 187-203, 1924), H. Geiger and A. Werner published the results of a redetermination by the scintillation method of the number of alpha-particles emitted per second from 1 gram of radium, and find this number to be  $3.4 \cdot 10^{10}$ . Although this value agrees with that originally found by E. Rutherford and H. Geiger (*Proc. Roy. Soc. (A)*, lxxxii. p. 141, 1908), it differs from the corrected value  $3.57 \cdot 10^{10}$  given by E. Rutherford (*Phil. Mag.* (6) xxviii. p. 320, 1914), and still more from that found later by the present writers, viz.  $3.72 \cdot 10^{10}$  (*Wien. Ber.* cxxvii. p. 405, 1918). In view of this discrepancy, perhaps we may be permitted to make some comment on Geiger and Werner's results, more especially as in our earlier work on this subject we also obtained results comparable with those of Geiger and Werner, and only after protracted experimenting and numerous improvements in our apparatus were we able to overcome

\* Communicated by the Authors.

the difficulties involved and arrive consistently at the higher figure. After careful consideration of the available evidence, we still feel that the value  $3.72 \cdot 10^{10}$  cannot be far removed from the true value, and we propose in what follows to state our main reasons for concluding that Geiger and Werner's value is too low.

*Radioactive Preparations.*

In consequence of the difficulties connected with the short life of  $\text{RaC}$ , Geiger and Werner decided in favour of small conical emanation containers with thin mica window, similar to those previously used in the Manchester laboratory, but of metal instead of glass. The conical part was of highly polished brass (vol. ca.  $10 \text{ mm.}^3$ ), silver-soldered at the apex to a fine platinum tube (bore  $0.1 \text{ mm.}$ , length ca.  $5\text{--}6 \text{ mm.}$ ), to which was fused at the remote end a glass capillary tube, which led to the emanation supply. After filling the small conical container with emanation and mixed gases at a pressure of a few cm., it was sealed off by fusing the glass round the remote end of the platinum tube, so that all the emanation was contained in the brass cone and the platinum tube (fractional volume ca. 1 per cent.). A small correction could be added to take account of this inoperative volume of the platinum tube.

To the present writers it appears that the use of such containers is open to question. As is well known, platinum usually contains quite an appreciable amount of occluded gases, which can be partially removed by heat, even in boiling water. On cooling the platinum in a gas-filled space, it will re-occlude gas, rapidly at first, and then more and more slowly with the lapse of time. Now the platinum in Geiger and Werner's emanation containers would necessarily become appreciably heated in the sealing-off operation, and perceptible quantities of occluded gas would enter the container, which was at reduced pressure. On cooling, the platinum will re-occlude gas from the container, and some of the emanation will disappear in this way. It is only necessary to assume that ca.  $1/20 \text{ mm.}^3$  (at N.P.T.) of the mixed gases disappear in this manner to account for the 10 per cent. discrepancy between the results of Geiger and Werner and our own, for whereas the occluded emanation will be partially effective in the emanation measurement, it will be wholly ineffective in the counting experiments. Although this effect may not be as large as 10 per cent., it is probably appreciable, and ought to be detectable by means of a gamma-ray electrometer.

Where continuous measurements are available, we have plotted as ordinate the number ( $Z$ ) of alpha-particles per 1 gm. Ra per sec., and as abscissa the strength of the preparation in millicuries. The average graph through the points for the RaC' determinations with preparations K and O (Geiger and Werner) are in conformity with the view that the emanation (and mixed gases) was removed (in addition to disintegration) at the rate of ca. 1 per cent. per day, and the RaEm determinations with preparations O and L, though less definite, also indicate a diminution with time. The remainder of their measurements are insufficient in number to apply this test. Whereas this might be accounted for by assuming that their mica window was not perfectly air-tight, it seems more probable that it can be explained by a slow occlusion by the platinum of the mixed gases in the emanation container. In view of this result, it seems feasible to suggest that several per cent. of the emanation was involved in the initial occlusion by the platinum on cooling (see previous paragraph).

It is rather unfortunate that Geiger and Werner in general only measured the Ra-equivalent of their preparations once, and then calculated the amount of emanation present later by using the known decay curve of the gas. Repeated measurement would have been valuable from the point of view of the above considerations.

It is interesting to note that their result with Em + A + C' ( $3.39_1 \cdot 10^{10}$ ) is about 1.6 per cent. greater than that ( $3.33_8 \cdot 10^{10}$ ) obtained by using RaC' alone. Whereas the emanation is contained in the volume of the container (which is at low pressure), the active deposit (RaA, RaB, RaC) will be buried in the walls of the vessel by virtue of recoil phenomena, and at depths varying from nil to the double range of the recoil atoms (RaA and RaB) in the material of the walls. Slight scattering and absorption effects would appear to be inevitable, and the correction for this is probably nearer 2 per cent. than 1 per cent., the amount suggested by Geiger and Werner.

#### *Scintillation Screens.*

Great care was taken by Geiger and Werner in the preparation of the material for their screens. They tested samples crystal by crystal and found that about 98 per cent. (590 in 600) gave scintillations with alpha-rays. Taking account of the size of the inactive crystals they estimate that their material would be about 99.6 per cent. efficient. These

tests, however, seem to have been made on loose material, and it is very doubtful whether they would have obtained similar efficacy had they tested the crystals after moistening, even with weak resin or turpentine oil, which substances were used as adhesives in coating the screens with zinc sulphide. It would appear very probable that the use of these binding agents will result in a diminution of the scintillating power of the material. It is a well-known fact that binding agents, even water-free varnishes, reduce the surface luminosity of zinc sulphide mixed with radioactive material emitting alpha-rays (luminous substance) to 30 per cent., and even less, of their original luminosity. This is certainly not due to a reduction of the intensity of the individual flashes so much as to a reduction of the number of effective hits.

Thus, in spite of their having estimated the percentage area of the surface of the screens uncovered by zinc sulphide, it is very doubtful whether Geiger and Werner are justified in assuming their screens to have 100 per cent. efficiency. Hitherto, a screen with an efficiency of 90 per cent. has been considered to have about an optimum of practicable efficiency.

#### *Method of Counting.*

The indirect method of estimating the true number of scintillations on the zinc sulphide screen, as used by Geiger and Werner, although ingenious, is certainly open to criticism. Their observations were made by counting simultaneously on the front and back faces of the screen. As different counts were obtained by the two observers, the legitimate assumption was made that observer I only sees a fraction  $\lambda_1$ , and observer II a fraction  $\lambda_2$  of the true number of scintillations ( $N$ ). Thus we have  $N_I = \lambda_1 \cdot N$ , and  $N_{II} = \lambda_2 \cdot N$ , and although these two fractions will, on the average, be fairly constant for the two observers, it is just as certain that the fraction for any one observer varies appreciably from day to day. A still greater element of uncertainty is introduced by their method of deriving  $N$  from these observations. The number of coincidences during a count is assumed to be  $C = \lambda_2 \cdot N_I = \lambda_2 \cdot \lambda_1 \cdot N$ , or  $C = \lambda_1 \cdot N_{II} = \lambda_1 \cdot \lambda_2 \cdot N$ , whence

$$N = \frac{N_I \cdot N_{II}}{C}.$$

Theoretically, this might be justifiable, if all the scintillations were of equal intensity, and if the dual registration of the scintillations were *instantaneous*; but in practice it is not. Geiger and Werner registered their counts on a chronograph



by electrical means, and using a tapping key each. Now a certain time lag occurs between the observation and the registration of a scintillation, which, as well as being different on the average for the two observers, will also depend on circumstances, such as fatigue, the frequency of scintillations, etc.; and what will happen when two or more scintillations occur simultaneously? Moreover, from our own observations, we know that each observer is slightly influenced by the tapping noise produced by the other observer during registration. It was for that reason that we, in our simultaneous counts, soon gave up the chronographic method of registration, and resorted to silent counting, the numbers being entered at definite periods by a third person.

From what has been said, it is clear that an appreciable latitude will be taken in estimating the number of coincidences, and almost unconsciously one will be inclined to regard as simultaneous, marks which lie approximately one over the other. The tendency will thus be to over-estimate the number of coincidences ( $\bar{C}$ ), and hence to under-estimate the value of  $N$ . This tendency will be greater, the greater the frequency of the scintillations, and would hardly be absent for the frequency of ca. 40 per minute, as used by Geiger and Werner.

It has been mentioned above that the factor  $\lambda$  would be expected to vary from time to time for each observer, and not necessarily in the same sense. In view of this, it is somewhat surprising to find (*loc. cit.* p. 196) the value of the factor for three different observers given to three places of decimals (viz. 0.884, 0.904, 0.917). These values have been derived from the total numbers of scintillations counted by each of the three observers working in pairs, and under different combinations. It would have been more interesting if a table had been constructed of the value of  $\lambda$  for each experimental series, and for each of the combinations of two observers. The accuracy to be expected in the determination of  $N$  would then have been more obvious, by consideration of the variation of  $\lambda$  for any one observer from one experimental series to the next. In consequence of such variations, the introduction of a third observer (and hence of a third value of  $\lambda$ ) into the series of measurements has probably been to reduce the accuracy attainable, if the total number (ca. 30,000) of scintillations had been counted by two observers only.

*General Remarks.*

Geiger and Werner suggest that the difference between their results and ours might be due to the presence of small electrometer kicks of secondary origin in our experiments, and they draw attention to our paper (*Wien. Ber.* cxxvii. p. 463, 1918) on the photographic registration of alpha-particles to support their contention. We cannot allow this remark to pass unchallenged. In the first place, the numerous experimental series on which we based our final result were performed by the subjective method of counting; in this the average magnitude of an electrometer kick was 10 scale divisions, and throws differing from this order of magnitude were absent, except for an occasional small throw due to vibration caused by passing traffic, and never larger than about 0.5 division. The photographic method was found less reliable under our conditions than the subjective method, and was hence abandoned.

Nevertheless, it is important to point out that, given a sensitive string electrometer of very small period, and using an alpha-particle frequency of say 40 per minute, the photographic method would be ideal for such work. Unfortunately, such an electrometer was not available for our work, and the Elster-Geitel electrometer was found to be too tardy in its action to give accurate results. The string required from 1 to  $1\frac{1}{2}$  seconds to return to its zero line after a kick, and 0.13 to 0.2 second to reach its maximum deflexion. This introduced difficulties in counting a rapid succession of alpha-particles in the counter; for if two particles followed each other within  $\frac{1}{5}$  sec. they were registered as a double throw, but if the second one occurred as the string was returning to its stationary position, the momentum it imparted to the string was partially counter-balanced by the counter-momentum already possessed by the string. It is clear that variable throws were thus obtained under such conditions by the photographic method, some of them relatively small humps on the already deflected record. But it is quite unjustifiable to suggest that these throws were due to secondary causes. They rendered such counts uncertain, and for this reason we abandoned the photographic method.

In view of the result obtained by Geiger and Werner, it is interesting to recall that, by the photographic method, and taking double kicks as single ones, we found a result identical with that of these authors. However, by applying Marsden and Barratt's formula to take account of the

occasional rapid succession of particles, we were able to conclude "from these experiments, that 'Z' must be greater than  $3.6 \cdot 10^{10}$ , and is probably not far removed from  $3.7 \cdot 10^{10}$ ." This is in good agreement with our visual counts by the subjective method of counting (viz.  $3.72 \cdot 10^{10}$ ), for which we can vouch a much higher degree of accuracy.

One of the most accurate methods of evaluating Z theoretically is by equating the kinetic energy of the alpha-particle and the recoil atom from radium to the thermal energy (in C.G.S. units) as obtained from accurate measurements on the heat production of radium. Using Geiger's value for the velocity of the alpha-particles from radium, and Hess's value for the hourly heat production from radium, we calculate for Z the value  $3.83 \cdot 10^{10}$ . This value is about 3 per cent. higher than that we obtained experimentally, but more than 10 per cent. greater than the result of Geiger and Werner. These authors conclude from their measurements that there can "hardly be any further doubt that in the radioactive transformation of the radium atom, apart from the kinetic energy of the alpha-particle and of the recoil atom, additional energy is liberated in consequence of the readjustments taking place in the atomic nucleus." As there are six such transformations between Ra and RaD, Geiger's results seem to involve that 6 times 3 or 18 calories per hour are to be ascribed to this extra liberated energy resulting from transformation, or 13 per cent. of the total measured heat production per 1 gram of Ra (plus Em, A, B, and C). This appears to be an exorbitantly high figure, particularly in view of the fact that the beta- and gamma-rays from Ra (B+C) respectively contribute only 3.4 per cent. and 4.7 per cent. of the total heat produced by radium and short-lived decay products. That there is a probability of liberation of extra energy during transformation we do not deny, but in our opinion the magnitude of such energy is more likely to be in accord with our own experimental results than with those of Geiger and Werner.

#### SUMMARY.

After careful examination of the whole of the experimental evidence, we are still of the opinion that the number of alpha-particles emitted per second by 1 gram of radium lies very near to  $3.72 \cdot 10^{10}$ , the value we obtained in 1918. In the present paper we state our reasons for believing that the value ( $3.40 \cdot 10^{10}$ ) recently obtained by Geiger and Werner, using the scintillation method, is too low. In connexion

with Geiger and Werner's work, the following points have been discussed :—

(1) It seems probable that after fusing off and allowing their emanation containers to cool, an appreciable fraction of the emanation would be occluded in the platinum lead-in tube of the container, and hence a corresponding fraction of the alpha-particles would be ineffective.

(2) Although the scintillating power of the zinc-sulphide crystals used in making the screens was tested, it is doubtful whether their efficiency is retained after they have been mixed with a binding agent, used as adhesive.

(3) Geiger and Werner's method of determining the true number of scintillations occurring in a given interval of time may readily lead to an under-estimate of this number, owing to the uncertainty in evaluating exactly the number of coincidences for the two observers.

The criticism of our photographic records raised by these authors has been shown to be irrelevant, as our final determinations were not performed by the photographic method.

The University,  
Graz.

The University,  
Sheffield.

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### XXIII. *Reflexion of Plane Polarized Light by Etched Metals.*

*By* MISS OLWEN JONES, *B.Sc.*\*

[Plate V.]

§ 1. **W**HEN plane polarized light is reflected normally from an etched metal surface, and the reflected light is analysed by a nicol prism, changes in the intensity of the light occur as the metal surface is rotated in its own plane. Under microscopic examination, changes in the individual crystals can be observed.

In the examination of the specimens, white light or the light of a mercury arc lamp was used—filters being sometimes employed. The light passed through an aperture in the side of the microscope tube and was reflected on to the metal surface by a glass slip. When plane polarized incident light was required, the polarizing nicol  $N_1$  was placed with its shorter diagonal parallel to the glass slip. In what follows the horizontal direction in which the light first enters the illuminator will be referred to as E and W. The incident electric vibrations for plane polarized incident light were therefore N and S. The analysing nicol  $N_2$  was attached to the eyepiece. When  $N_2$  is placed so as to extinguish the light travelling up the microscope tube, if no change of

\* Communicated by Mr. J. H. Shaxby.

polarization occurs on reflexion (*e.g.* normal reflexion at a polished surface), the nicols are virtually crossed and are referred to as such. Similarly they are virtually parallel when  $N_2$  is rotated through  $90^\circ$  from the crossed position.

The metals examined included steels, brasses, aluminium-bronzes, and copper-nickel, also pure metals—copper, bismuth, nickel, and aluminium. They were polished and etched in the usual way. Nitric acid was most frequently used, and for copper alloys a solution of ferric chloride and hydrochloric acid. The reagents are referred to in the course of the paper.

§ 2. Very lightly etched specimens of steel were first examined exhibiting well differentiated pearlite and ferrite structure. On rotation of the stage under crossed nicols the ferrite remained uniformly dark, but the pearlite underwent changes passing through four maxima and four minima in a complete revolution. The pearlite showed the usual striated structure, and it was observed that the minima, which were in general complete extinctions, occurred when the striations were either E and W or N and S in the field, *i.e.* either in, or perpendicular to, the plane of polarization of the incident light.

Fig. 1.

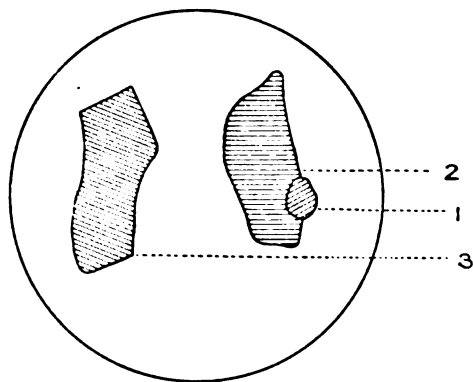


Fig. 1 gives the approximate orientation of three pearlite grains when the stage reading was  $44^\circ$ . The stage readings for the minima of three crystals were:—

(1) .....	$17^\circ$	(striations horizontal)	$106^\circ$	$196^\circ$	$283^\circ$
(2) .....	$44^\circ$	( „ „ )	$133^\circ$	$223^\circ.5$	$322^\circ$
(3) .....	$69^\circ.5$	( „ „ )	$160^\circ$	$251^\circ.5$	$339^\circ$

The minima therefore occurred at intervals of  $90^\circ$ .

Between the minima the crystals brightened up considerably and gave maxima when the striations were inclined at  $45^\circ$  on either side of the N and S line. The same specimen was examined with the nicols parallel. When the stage was rotated the ferrite remained uniformly bright, while the pearlite went through two maxima (striations N and S) and two minima (striations E and W).

A specimen of Muntz metal (30 per cent. Zn, 70 per cent. Cu) was lightly etched with nitric acid. It exhibited the usual duplex structure—the larger crystals of the  $\alpha$  phase and the smaller complex laminated crystals of the mixed  $\beta$  and  $\gamma$  phase. When examined under high power, faint striations were visible in the second group of crystals but not with  $\alpha$  crystals. On rotating the stage under crossed nicols the second group underwent the series of changes noted in the pearlite, while most of the  $\alpha$  crystals remained uniformly dark. On etching more deeply with nitric acid, however, the  $\alpha$  crystals went through the four maxima and four minima in a complete revolution, and on examination under high power showed faint striations. The striations in both sets of crystals were N-S or E-W in the minimum positions.

Pure copper was lightly etched with ammonia and examined. Individual crystals showed the four maxima and four minima. On etching more deeply with nitric acid and examining under high power, the striations in the crystals became distinct and the directions in the field of these at the maxima and minima were exactly as before; also on examining under parallel nicols, the maxima occurred when the striations were N-S and the minima when they were E-W, *i. e.* two maxima and two minima, as in the steel\*.

Similar results were obtained in the case of bronze (10 per cent. Al). A specimen of bismuth lightly etched with nitric acid showed several crystals with well marked maxima and minima, the stage readings for a characteristic grain being

Minima .....	159°	247°	339°	67°
Maxima .....	205°	296°	26°	114°

\* In several of the above cases it was at first thought that one pair of maxima (separated by  $180^\circ$ ) was brighter than the other pair, *e. g.* with a certain bismuth crystal two maxima (at  $303^\circ$  and  $123^\circ$ ) were much brighter than the other two (at  $213^\circ$  and  $30^\circ$ ). The minima were not completely dark and their positions ( $70^\circ$ ,  $173^\circ$ ,  $251^\circ$ , and  $350^\circ$ ) did not bisect the angles between the maxima. Similar effects were sometimes observed in other specimens. They were traced to inaccuracy in

A lightly etched brass examined under parallel nicols showed some crystals remaining uniformly bright and others with two maxima and two minima. Under crossed nicols the first set remained constantly dark, the second set again showing four maxima and four minima.

If light was allowed to fall directly on the crystal from the side (ordinary oblique illumination) and no nicols used, there were two maxima and two minima.

The readings for a single crystal under various types of illumination are :—

(a) *Under parallel nicols.*

Maxima .....  $231^{\circ}$                        $50^{\circ}$  (not sharply defined).

Minima ..... Not sufficiently sharp to be determined with any degree of accuracy. Approximately half-way between the maxima.

(b) *Under crossed nicols.*

Maxima .....	$180^{\circ}$	$272^{\circ}$	$0^{\circ}$	$90^{\circ}$	
Minima .....		$227^{\circ}$	$317^{\circ}$	$46^{\circ}$	$135^{\circ}$

(c) *Oblique incidence.*

Maxima .....  $225^{\circ}$                                        $45^{\circ}$

Minima ..... Very little light reflected at any position between the maxima.

The photographs in Pl. V. are of aluminium bronze + 2 per cent. phosphorus (spec. 8).

In the first pair, *a* shows the appearance with unpolarized light, *b* with crossed nicols in one particular orientation.

The 2nd and 3rd pairs with crossed nicols illustrate the effect of rotating a specimen through  $45^{\circ}$ ; the maxima in *a* pass into the minima in *b*, and *vice versa*.

§ 3. The most interesting specimen examined (No. 8) was of composition Cu 94.8 per cent., Al 5 per cent., P 0.2 per cent. In addition to the maxima and minima it showed

the setting of  $N_2$ . For an exactly crossed position of  $N_2$  (as tested by complete extinction of light reflected from a polished surface) the maxima were of the same intensity and separated from each other by  $90^{\circ}$  and from adjacent minima by  $45^{\circ}$ . If  $N_2$  was then displaced very slightly to one side or the other one or other pair of maxima brightened up considerably, the other pair becoming correspondingly darker. In fact this affords quite a sensitive means of setting the nicols accurately in the crossed position.

very striking colour changes with the rotation of the stage or of  $N_2$ .

When very lightly etched with ferric chloride and hydrochloric acid and illuminated in the ordinary way without polarized light, the different crystals were only distinguished with difficulty and there were no signs of fine structure. The surface showed a large number of pits which under high power were seen to be partially flowed over by the surface film in the manner described by Sir G. Beilby.

On examination under crossed nicols the individual crystals were at once clearly differentiated, being of various degrees of brightness. The crystals were large and irregular and without the usual sharp corners. Each went through four very sharp maxima and minima in a complete rotation. With uncrossed nicols there were again two maxima and minima, these not being very well defined.

The following readings were taken for an individual crystal:—

(a) *Crossed nicols.*

Maxima .....	268°	354°	83°	173°
Minima .....	313°	43°	130°	223°

(b) *Uncrossed nicols.*

Maxima .....	315°	135°
--------------	------	------

As the stage was rotated under crossed nicols each crystal went through a definite colour series. The colours were much more marked if  $N_2$  was shifted slightly from its crossed position.

If the stage was fixed so that a given crystal was at 45° from a minimum under crossed nicols and then  $N_2$  was rotated slightly in, say, a clockwise direction, the reflected light became red. If  $N_2$  was rotated slightly in an anticlockwise direction the light became green. The same colour changes occurred with the stage rotated through 180° from this position, while if the stage was turned through 90°, clockwise rotation of  $N_2$  produced the green and anticlockwise rotation produced the red.

Similar colour changes were also observed in some specimens of 95 per cent. Cu, 5 per cent. Al, but the general effect was much less marked.

The origin of the colours is not at present clear. The brilliant effects noted in specimen 8 appear to depend a great deal on the depth of etching and the reagent used, and



are obtained with difficulty. An increase of the red or the green on rotation of  $N_2$  at a maximum can be more frequently distinguished, although it is closely allied to the whole effect noted in 8.

The colouring is quite distinct from ordinary tarnishing, as tarnished specimens showing bright colour under ordinary illumination have been examined and do not show the colour sequences under crossed nicols, often appearing quite dark.

The effect apparently depends on the polarization of the light. Specimen 8 was subsequently etched more deeply with nitric acid and examined. The brilliant effects were no longer present but slight colour appeared in parts. These parts were often still covered with a thin surface film of the metal. Several of the crystals showed very regular striations under high power.

§ 4. The observation of the maxima and minima with crossed and uncrossed nicols led to the conclusion that the production of the maxima and minima might be due to two successive reflexions at the metal surface. The azimuths of the maxima and minima were constant over the whole crystal surface even when this was very large. Thus, a bar of aluminium, which was kindly sent by Prof. H. C. H. Carpenter, contained some crystals measuring approximately 1 in. or  $1\frac{1}{2}$  in. across and the appearances were the same over each whole crystal. The phenomena are obviously therefore due to the internal structure of a crystal disclosed by etching.

It has already been shown by several workers that a single crystal of a metal consists in general of similarly oriented parts. In the Bakerian Lecture of 1899 on the "Crystalline Structure of Metals," by Sir J. A. Ewing and Professor Rosenhain, it is stated that :

"Each grain is built up of similarly oriented parts but the orientation changes from grain to grain. Etching a polished surface develops a multitude of facets which have the same orientation over the surface of any one grain but different orientations in different grains" (Phil. Trans. vol.193, p. 356).

The behaviour of polarized light would point to the fact that the surfaces of some of the crystals are really *furrowed*, i. e., there are two sets of parallel faces reflecting light and not only one as is the case in the strained crystals described in the above paper (p. 363).

This supposition is supported by the fact that with obliquely incident light the crystals in general appear

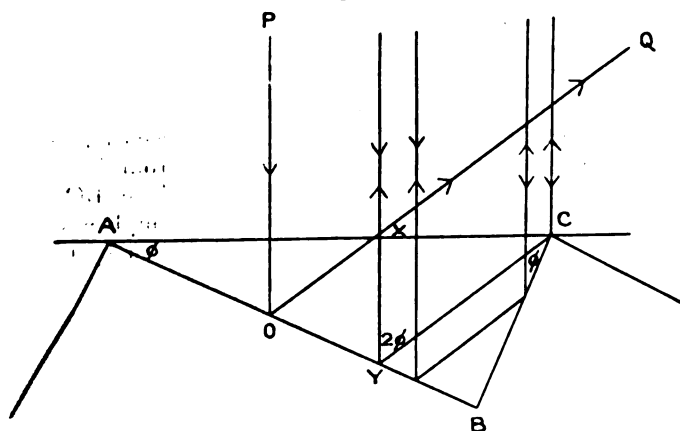
brightly illuminated at two positions (separated by  $180^\circ$ ) in a complete revolution of the stage. Most of the large aluminium crystals which can be examined individually without the microscope also show two positions for the maximum reflexion of obliquely incident light. Measurements of the direction of maximum reflexion at the two maxima showed that the two sets of planes were inclined at  $90^\circ$  or a few degrees more or less. Since the etched crystals reflect normally incident light, either

- (a) the etching has not been deep enough completely to remove the surface film—giving a polished surface effect *e.g.* in the ferrite grains of lightly etched steel; or
- (b) the exposed furrows must have their faces inclined at an angle of approximately  $90^\circ$  since the light returns along the incident path.

A certain amount of deviation from  $90^\circ$  would be possible as the objective would gather in rays of small deviation.

§ 5. Suppose that a vertical section of an etched crystal is as in fig. 2. Vertical rays incident along AY will not be

Fig. 2.

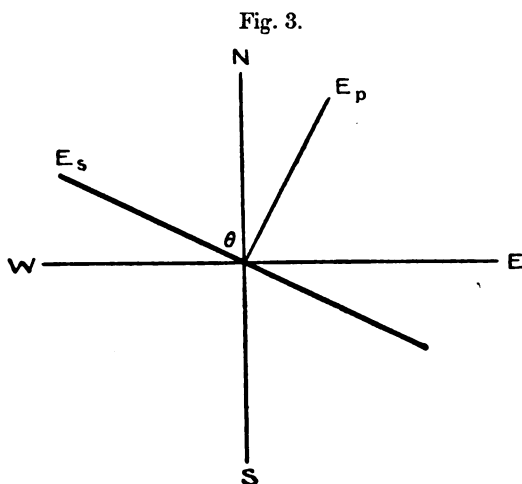


reflected at CB and so will be lost, *e.g.* ray POQ. The proportion of the surface therefore which is effective if only rays finally reflected vertically are considered, is

$$\frac{CX}{CA} = \frac{CA \sin \phi \sin 2\phi}{CA \cos \phi} = 2 \sin^2 \phi,$$

where  $\phi$  is the inclination of the longer side to the horizontal.

Let the vertical incident light be plane polarized in a direction such that the incident vibrations (electric vectors) make an angle  $\theta$  with the lines of intersection of the slant surfaces as in fig. 3, which represents the field of view. Let  $E_p$  and  $E_s$  ( $E$  being the amplitude of the incident light, fig. 3) be the components of amplitude of the incident light in and perpendicular to the plane of incidence on such a surface as AB (fig. 2) (*i. e.* polarized perpendicularly to and in the plane of incidence respectively).



Let  $\phi$  = angle of incidence and  $R_p, R_s$  be the corresponding amplitude components of the light reflected from AB.

This light then falls on the second surface BC at an angle  $\phi'$ . Let  $R_p, R_s$  be the final reflected amplitude components. The usual optical theory of reflexion by metallic surfaces gives

$$R_p = E_p \frac{\tan(\phi - \chi)}{\tan(\phi + \chi)} = E \sin \theta \frac{\tan(\phi - \chi)}{\tan(\phi + \chi)}$$

and

$$R_p = E \sin \theta \left\{ \frac{\tan(\phi - \chi)}{\tan(\phi + \chi)} \right\} \left\{ \frac{\tan(\phi' - \chi')}{\tan(\phi' + \chi')} \right\} = K_1 \sin \theta.$$

Similarly,

$$R_s = E \cos \theta \left\{ \frac{\sin(\phi - \chi)}{\sin(\phi + \chi)} \right\} \left\{ \frac{\sin(\phi' - \chi')}{\sin(\phi' + \chi')} \right\} = K_2 \cos \theta.$$

$K_1, K_2$  being constants as far as amplitudes are concerned,

since in a given crystal as the stage is rotated  $\phi$  and  $\phi'$  remain the same.

The resultant amplitude  $R$  along the  $EW$  line (*i. e.* the direction of vibrations transmitted by the analyser) is then given by resolving  $R_p$ ,  $R_s$  in that direction, *i. e.*

$$R = (K_1 - K_2) \sin \theta \cos \theta = \frac{1}{2}(K_1 - K_2) \sin 2\theta.$$

Hence the intensity is a maximum when

$$2\theta = \frac{\pi}{2} \text{ or } \frac{3\pi}{2},$$

$$\text{i. e. } \theta = 45^\circ \text{ or } 135^\circ,$$

and no light will be transmitted when  $\theta = 0^\circ$  or  $90^\circ$ .

Hence maxima occur four times in each revolution in accord with the observed phenomena.

With parallel nicols  $N_2$  transmits light along the  $NS$  line. Therefore the resultant

$$\begin{aligned} &= K_1 \sin^2 \theta + K_2 \cos^2 \theta \\ &= K_2 - (K_2 - K_1) \sin^2 \theta. \end{aligned}$$

This gives maxima or minima at  $\theta = \frac{n\pi}{2}$ ;

$$\text{at } \theta = 0^\circ \text{ or } 180^\circ, \quad R = K_2,$$

$$\text{at } \theta = 90^\circ \text{ or } 270^\circ, \quad R = K_1.$$

$$\text{Here } K_2 > K_1.$$

Hence maxima occur when the join of the slant surfaces is parallel to the incident vibrations and minima when it is perpendicular thereto, *i. e.* 2 maxima and 2 minima in a complete rotation.

With a view to obtaining a comparison of effects, blocks of metal were set up to represent the "furrows," the angle between the faces being  $90^\circ$ . This was done with pairs of blocks of copper, bismuth, brass, nickel, and copper-nickel, and the furrows examined under the same conditions as the crystals.

In all cases they showed the same maxima and minima as the crystals, the directions of the furrows corresponding to the directions of the striations in the crystals. The effects were independent of the use of lenses in examination.

Further evidence that the cause of the polarized effects was to be found in the furrowed nature of the surface was

afforded by scratches which under crossed nicols showed bright maxima when at  $45^\circ$  on either side of the plane of incident polarization. A ruled metallic grating was also examined under the same conditions and showed very well marked maxima and minima, the minima again occurring when the lines were in or perpendicular to the plane of incident polarization and the maxima at  $45^\circ$  on either side.

In conclusion I wish to express my indebtedness to Mr. J. H. Shaxby for valuable help and advice throughout the course of the work, to Mr. C. Handford for assistance in the preparation of some specimens, and to Prof. A. A. Read and Prof. H. C. H. Carpenter for providing us with some of the specimens examined.

### *Summary and Conclusions.*

Etched metal surfaces were illuminated by normally incident plane polarized light and the reflected light passed through a nicol prism.

If the analyser is placed so as to extinguish the light reflected from a polished part of the surface ("crossed" nicols) the etched parts show various degrees of brightness according to the orientation of the crystal. As the surface is rotated through  $360^\circ$  in its own plane each etched crystal exhibits 4 maxima and 4 minima. If the analyser is turned through  $90^\circ$  the crystals give 2 maxima and 2 minima.

In some crystals showing the above effects it was possible to distinguish a fine striated structure of the surface under high magnification (1800 in some cases).

The view is put forward that the maxima and minima are due to the similar orientation of the parts making up any one crystal grain. This regular orientation is developed by etching into a ridged or furrowed structure of the surface, producing the striated appearance seen under high powers. Hence light incident normally on the surface of such an etched specimen is returned after two reflexions, one at each face of a furrow. The state of polarization of such light is shown to account for the maxima and minima.

Confirmatory observations were made by setting up large-scale models of such furrows by means of polished blocks and by examining scratches and the rulings of a metallic grating.

Viriamu Jones Physical Laboratory,  
University College, Cardiff.

FIG. 1 *a*.



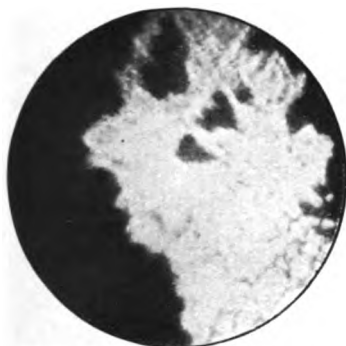
→  
× 25.

FIG. 1 *b*.



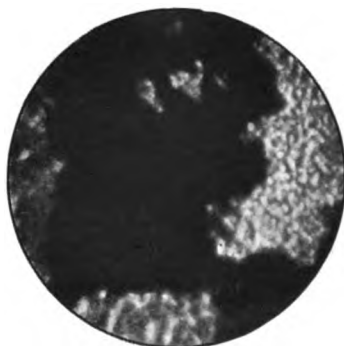
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× 25.

FIG. 2 *a*.



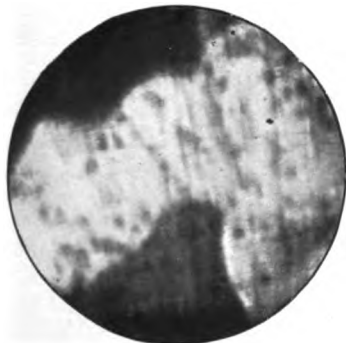
→  
× 25.

FIG. 2 *b*.



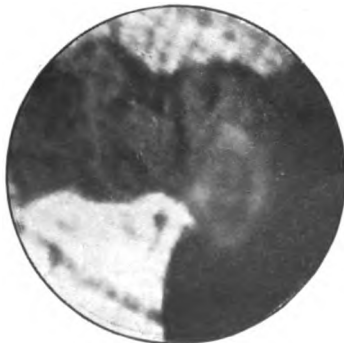
→  
× 25.

FIG. 3 *a*.



→  
× 100.

FIG. 3 *b*.



→  
× 100.



XXIV. *A Registering Micro-Photometer for Accurate Measurements.* By Prof. MANNE SIEGBAHN, D.Sc.\*

FOR many purposes, especially in the spectroscopy of ordinary light and X-rays, a registering micro-photometer is needed. A photometric registering of a spectral plate in many cases shows a great deal more than can be seen directly on ocular viewing of the plate. Also an erroneous conclusion, caused by the physiological impress for instance through the contrast effect, may be avoided. There have also been constructed and used a variety of different micro-photometers, both of automatic registering type and also for subjective work, with this motive. Some years ago the author† built an automatic registering apparatus, where a fine pencil of light, after passing the photographic plate, fell on a thermopile, whose electromotive force was then registered with the help of a galvanometer and a drum. The drum and the photographic plate were moved through different gears driven from one and the same motor. But a registering in this way could not be used for more accurate measurements when it was wanted that a certain distance on the registering drum should correspond to a definite distance on the plate. A difference in the tension of the straps causes, of course, an alteration of the relation between the two distances.

Considerably better results were afforded by a later construction ‡, where a steel band connected the registered plate with the registering drum. In this apparatus the tension of the steel band was held constant during the registering by a load acting on the drum. Some inconvenience, which it is not necessary to mention now, caused me to construct a new model, which it was hoped would also be able to give still greater accurateness in the measurements. This apparatus, of which I will now give a short description, is very convenient in use, and enables measurements of line-distances to be made with a precision of about 0.002 mm.

From the three figures (figs. 1-3) the construction and working of the instrument may be seen. The plate to be photometered is placed horizontally on the slide B. This slide consists of two micrometrically adjustable parts, where the displacement of the photographic plate can be read directly to 1/100 of a millimetre and the thousands may be estimated. When the photometer is used for the registering

\* Communicated by the Author.

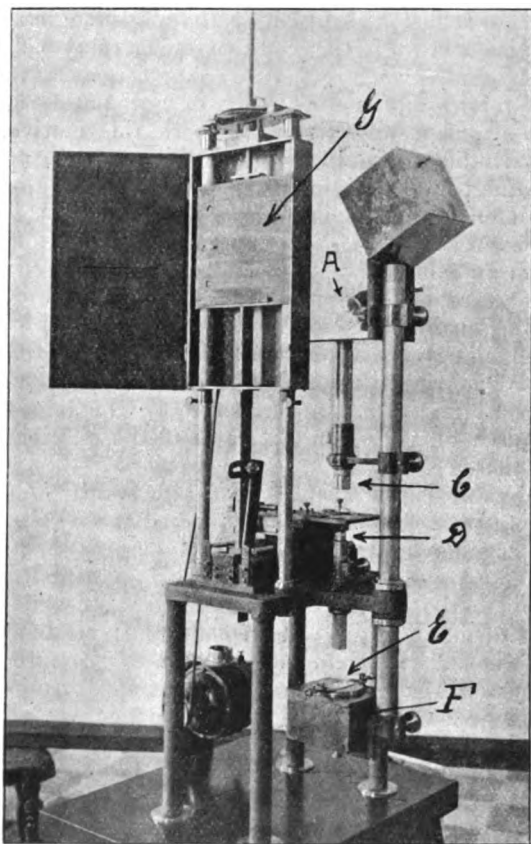
† *Phil. Mag.* May 1914, p. 910; *Ann. d. Phys.* 1913, p. 689; Malmer, Diss. Lund, 1915.

‡ Described by Lindh, *Zs. für Phys.* vi. p. 303 (1921).



of plates, this arrangement is intended to enable different parts, say, of a spectral line to be set in for the registration. For subjective use of the photometer through observation of the deviation of the galvanometer, the micrometer screws may be used for measuring the distances for instance between the blackening tops of two lines.

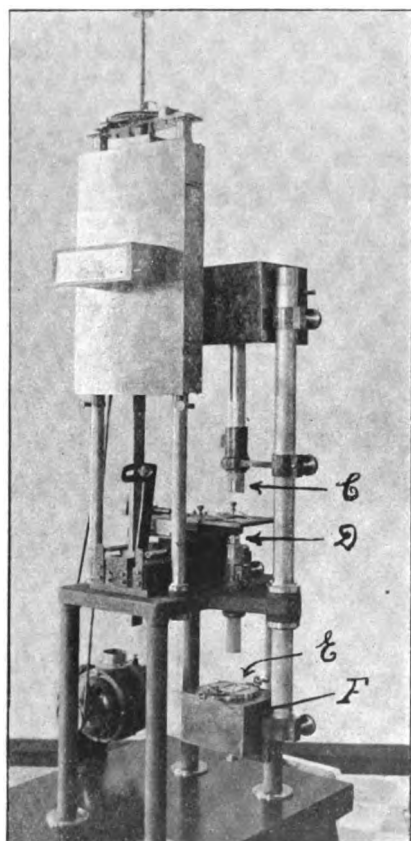
Fig. 1.



The optical part of the instrument consists of (1) an auto-lamp A (for 6–12 volts) with a straight spiral wire, (2) a condenser C, (3) an objective D, and (4) a micrometrically adjustable slit E. With the help of the condenser an image of the filament is thrown on the photographic plate. With the coated side of the plate turned down, an image of the film is formed on the slit. This operation is best done in the following way:—The condenser is lowered a little to get a greater portion

of the film illuminated. Then the objective is moved until a sharp image of the grains in the film is seen on a white paper gummed on the slit-backs. Also it is adjusted so that spectral lines are exactly parallel with the slit. After this is done the condenser is moved back to the place where a good image of the filament on the film is received. This last step may also, and with better results, be made through observing on the galvanometer when the maximum deviation is obtained.

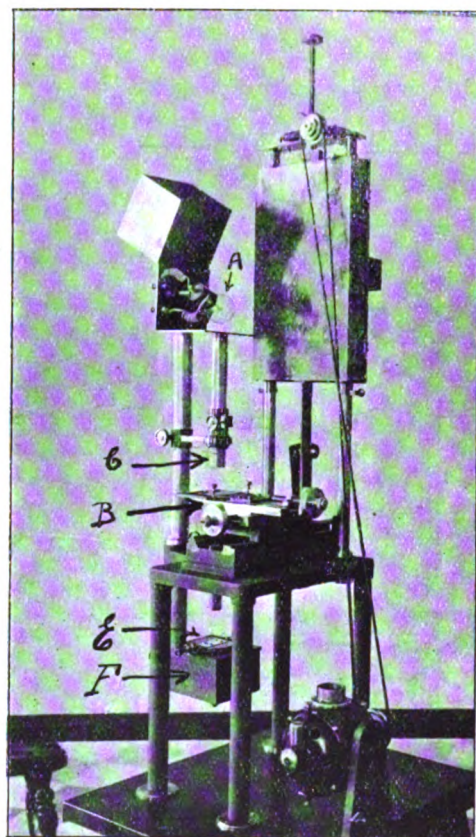
Fig. 2.



The slit-width, divided by the magnification of the objective, gives approximately the breadth of the part of the photographic plate which is registered. A magnification of about 10 times may be convenient, and with a slit-width of 0.2 mm. a band of about 0.02 mm. is cut out of the photographic plate. As to the length of the registered

band, this was in most cases here described about 1.5 mm., as the slit and the thermopile had a length of 15 mm. Naturally, a rectangular portion of these dimensions, that is  $1.5 \times 0.02$  mm. of the photographic plate, shows irregularities in the blackening, owing to the accidental arrangement of the

Fig. 3.



grains in the film. On working with such small areas it is therefore necessary to make registrations on different parts of the spectral lines, and then to take a mean of many such curves. With four different registrations the accidental errors caused by the grains may be eliminated, as is shown in a paper by Mr. Larson and the author\* where we used the apparatus to find the structure of some complicated X-ray

\*Siegbahn and Larson, *Arkiv f. Mat. Astr. o. Fysik*, Stockholm, 1924.

spectral lines. As we then worked with plates having rather large grains, a smaller number of registrations may be sufficient on using plates with finer grains.

To get a stable zero-point of the galvanometer, it was necessary to have an effective shield for the thermopile F. For this purpose the thermopile was placed in a heavy copper cylinder, and then this cylinder was enclosed airtight in a second box.

The most important part of the photometer is the arrangement by which the holder for the registering plate is connected with the slide for the registered plate. As the photometer was constructed with a view of enabling accurate measurements of distances on the *registrations*, it was necessary to use photographic plates instead of paper or film for registration of the galvanometer deflexions. These plates are fixed on a carrier G, which can be moved vertically and exactly on two steel bars of circular section. A third steel bar of rectangular cross-section is fixed to the carrier, and on the lower part of this one another similar steel bar is attached, as seen on fig. 1. The angle between these two steel bars may easily be varied as desired. When the carrier for the plate is going downwards, the wedge, formed by the last two steel bars, is pressed down between two agate cylinders, of which one is fixed to the bed and the other attached to the horizontal slide. Provided the two steel bars have *exactly straight* sides, a certain *vertical* displacement of the carrier G will correspond to a definite *horizontal* displacement of the movable slide carrying the plate.

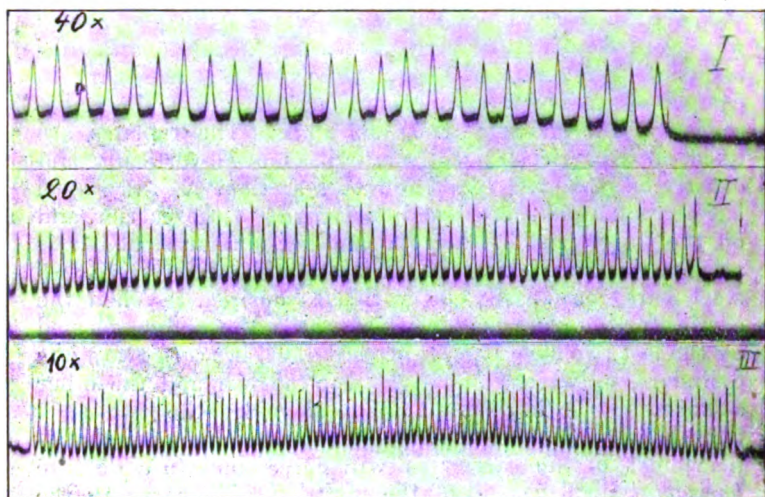
The arrangement to give the slow motion of the registering parts is seen on the upper side of the box for the vertical carrier. A heliacal screw acting on a nut brings down the rotation velocity of a small motor to a convenient amount. With the galvanometer and thermopile used in this apparatus the registration of a curve took about 5 minutes.

Some tests of the instruments may be given. The first of them was made in the following way:—An ocular scale as commonly used in microscopes, with a hundred divisions in 10 mm., was placed on the horizontal slide, and in the ordinary way photometered with three different wedge angles. These three angles were adapted to give a magnification (that is, the relation of the vertical to the horizontal motion) of about 10, 20, and 40. The three curves are seen in fig. 4. A measurement of the distances between the peaks gives values which do not differ from one another more than may be ascribed to dividing faults in the ocular scale. Eliminating these faults, the exactitude of the distances as measured on

the registered plate stays within 0.0025 mm. reduced to the distance on the scale.

It may be mentioned that the exactitude is determined principally by the precision with which the sides of the two steel bars are made. A still higher precision may certainly be attained if the steel bars are made with greater care than was the case in this instrument. For our purposes an accuracy of 0.0025 mm. was quite sufficient.

Fig. 4.



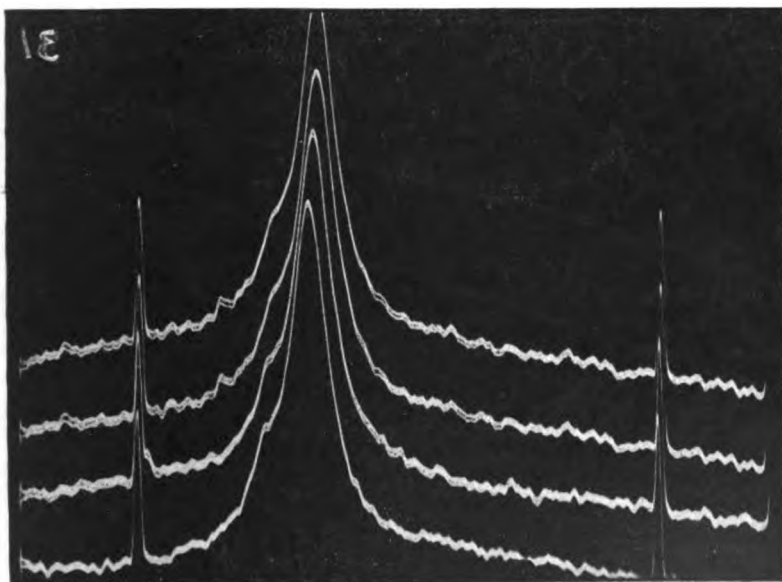
From the same figure it may be seen that the breadth of the scale lines is about  $\frac{1}{3}$  of the distance between the scale divisions. This corresponds to about 0.03 mm. as the width of the rectangular area cut out on the glass scale. As the magnification of the objective was about 10 times, this corresponds to a slit-width of 0.3 mm. Regarding this point, it is of interest to note that the image of the filament of the lamp is much broader. It shows that it is not at all necessary to use a special slit instead of the filament—as has sometimes been proposed—to get a good definition of the registered lines.

From the same figure it may also be concluded that the separation in this case was such that the two lines with a distance of 0.03 mm. will be wholly separated, and if the distance varies down to 0.015 mm., the curve will show a groove between the two peaks of the middle of the lines. There are no difficulties in getting a somewhat higher resolution than was given in this case, where the very short scale lines were used. With longer lines a finer slit could be used,

still giving the same total deviation. Also it is possible to give the lamp more current, which enables a further reduction of the slit-width without reducing the galvanometer deflexion.

As an illustration of the working of the registering apparatus, fig. 5 shows a plate taken from a rather complicated X-ray spectral line (Mo-L $\alpha$ ). Of the four curves the two uppermost are taken on the same place of the spectral plate. It will be seen that all the small deviations are exactly of the same shape in both these curves, showing that they are caused by small irregularities in the plate owing to the grains. The two other curves were taken after the spectral plate had been displaced a little parallel to the spectral lines.

Fig. 5.



As we said above, it is easy from some such curves, taken on different points of the spectral lines, to eliminate the accidental irregularities. The sharp peaks on both sides of the complicated spectral line are due to two lines scratched on the film with a sharp edge. They serve to determine the magnification when their distances on the spectral plate and on the registered plate are measured with a comparator.

It may be mentioned that an attempt was made, with the view of getting an automatic levelling of the irregularities caused by the grains in the film. As the spectral lines are rather long, an extension of the measured area in the



direction of the lines is possible. With the breadth still the same, the definition should be as good as before, but the irregularities strongly suppressed. This was done with the help of two cylindrical lenses shut in, the one between the condenser and the plate, and the other between the plate and the objective. But the result was not very good, as it is difficult to make the adjustments of the optical system accurate enough; also the loss of intensity was rather great.

In the experiments described above, Mr. Erik Bäcklin has in a very skilful way assisted me. I wish to express here my hearty thanks for his valuable help.

Upsala, Physical Laboratory of the University,  
March 17, 1924.

XXV. *On the Measurement of very small Changes of Capacity.*  
By ROSS GUNN, B.S.E.E., M.S., Instructor in Physics,  
Yale University\*.

THE ultra micrometer has proved of great value for the measurement of certain physical quantities, and while the methods of Whiddington (Phil. Mag. Nov. 1920) and Dowling (Phil. Mag. July 1923) give results, they leave much to be desired from the point of convenience, stability, and sensitivity. The writer would like to suggest two methods that are direct reading and very easy to use.

The method which will be described first is an extremely simple one, but is quite sensitive, giving a change of one microampere for a capacity change of  $10^{-15}$  farad. By increasing the frequency and being careful with the design of the electrical circuits, this may be improved considerably.

The essential features of the circuit used are shown in fig. 1. The radio frequency oscillator A should be capable of delivering three or four watts at a frequency of about 1,500,000 cycles. The anode coil of the oscillator  $I_1$  is coupled *loosely* to the coil  $L_2$ , which, together with the capacity to be measured,  $C_2$ , makes an oscillating circuit. This circuit, in which the losses should be kept as low as possible, is connected with another vacuum tube, as shown in the diagram. The grid biasing battery  $B_1$  should have a potential of at least one-third that of the anode battery  $B_2$ . In general this will be more than sufficient to reduce the anode current to zero, when there is no impressed A.C. voltage in the circuit  $L_2C_2$ .

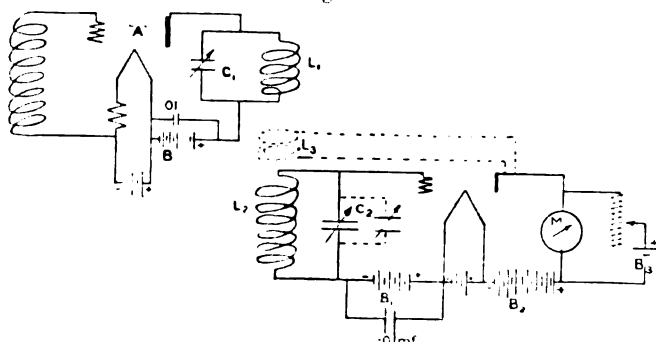
The sensitivity is somewhat greater when the impressed A.C. potential is sufficient to cause an anode current of about

\* Communicated by the Author.

100 microamperes. The battery  $B_3$  and resistance  $R$  are used to balance out this current if it is found desirable when using a very sensitive direct current microammeter or galvanometer.

To adjust the arrangement, place a shunt across the microammeter so that two or three milliamperes will give full scale deflexion. Tune the oscillator  $A$  by slowly changing  $C_1$  until resonance is reached in the circuit  $L_2C_2$ , which condition will be indicated by a current through the meter.

Fig. 1.



Loosen the coupling between  $L_1$  and  $L_2$  and remove the shunt from the meter. The most sensitive point will be found by adjusting the coupling so that a current of approximately 100 microamperes flows when the circuit  $L_2C_2$  is adjusted to a point just off of resonance.

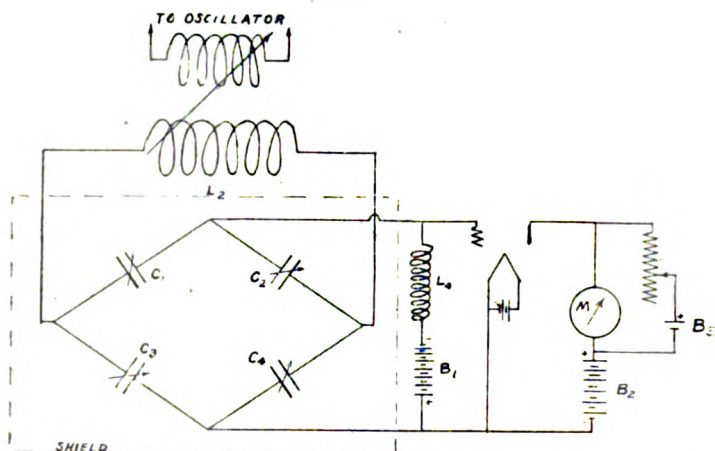
With this simple arrangement it is often possible to feed some of the anode energy back into the grid circuit with a considerable increase in sensitivity. One method of doing this is by means of the coil  $L_3$ , but in general it is hardly worth while, as the circuit is essentially an unstable one.

The second method (shown in fig. 2) is closely related to the one described above, for a capacity bridge replaces the single condenser formerly used. If the bridge and the coupling coil  $L_2$  be so adjusted that they resonate approximately with the impressed frequency, and if one of the capacity arms of the bridge be changed, it is obvious that the potential impressed on the grid of the output vacuum tube will change, for two reasons: first, the usual variation caused by the changing of the impedance of the bridge-arms; and second, the variation due to tuning, as in the first case. It is then apparent that the most sensitive condition is realized when the bridge itself is not balanced. The diagram shows the arrangement of the various parts, and needs little explanation, as the details will occur immediately to the reader. It is



evident that the proper adjustment will require some skill, as there are two conditions to be satisfied simultaneously for maximum sensitivity.

Fig. 2.



It will be necessary to shield the bridge both from the surroundings and the associated tubes. With the arrangement used by the writer, the approach of a person within several feet produced a current change of a few microamperes. Shielding and proper arrangement of the parts eliminated this, and it was easily possible to obtain a sensitivity of one microampere for a capacity change of the order of  $10^{-18}$  farad. This was accomplished by using a frequency of 1,500,000 cycles and capacities in the bridge of 125 micro-microfarads. Some attention must be given to keeping the distributed and stray capacities as low as possible.

## XXVI. Notices respecting New Books.

*The Calculus of Observations. A Treatise on Numerical Mathematics.*

By E. T. WHITTAKER, Sc.D., F.R.S., Professor of Mathematics in the University of Edinburgh, and G. ROBINSON, M.A., B.Sc., Lecturer in Mathematics in the University of Edinburgh. (Pp. xvi+395.) (London: Blackie & Son, 1924. Price 18s. net.)

THIS volume deals with the mathematical problems which arise in dealing with numerical data. Such problems are met with in many branches both of pure and of applied science, in astronomy, in meteorology, in physics and in engineering, for example. The statistician, the biometrician, and the actuary have also constantly to deal with them. In spite of the great practical importance of

the subject, it has been almost entirely neglected in the mathematical courses given at the various British Universities, with the exception of the University of Edinburgh, where Prof. Whittaker has given courses on the subject for the past ten years. These lectures form the basis of the present volume. All those who have to deal with masses of numerical data will be grateful to the authors for having expanded the substance of the lectures into book form. A wide range of subject matter is dealt with, including interpolation, central difference formulæ and their applications, the numerical solution of equations, numerical integration, error laws and the method of least squares, Fourier analysis, the smoothing of data, correlation and periodogram analysis.

Much of the material which is here gathered together was not readily accessible to the average student. Particular reference may be made to a valuable method for smoothing data, due to Prof. Whittaker himself, in which the degree to which fidelity to the original data may be sacrificed in order to obtain smoothness may be varied according to the nature of the problem.

The treatment throughout is lucid and rigorous and is illustrated by many numerical examples. The one criticism which we have to offer is that many of these examples deal with integral numbers or coefficients, which do not usually occur in practice. Thus the methods given, for example, for the solution of the normal equations in the method of least squares and for the determination of the weights of the several unknowns are not those which the practical computer would normally use.

The volume ably fills a notable gap in mathematical literature. It may be noted that the first four chapters are also published separately with the title 'A Short Course in Interpolation.'

*Report on Radiation and the Quantum Theory.* By Dr. J. H. JEANS.  
(2nd Edition.) (Fleetway Press. 7s. 6d. net.)

PERHAPS no book on modern physics has been awaited more eagerly. Dr. Jeans always gives a fair and logical presentation of the case for and against any theory, and in this instance, as one of the pioneers whose work is too often passed over in current writings on spectra, is peculiarly fitted to do so. It is very essential that original writers in this country should not confine their writings to papers in scientific journals; for our share in the modern march of physics is being lost sight of, or ignored, even among those who, in a national sense, are the chief exponents at present, even in our language. Perhaps this consideration should be emphasised no further, for there is no doubt in the mind of a reader of Dr. Jeans' Report as to the position of the subject at present. It is a final account of the theory as it exists to-day. But we must recommend readers to compare his Report with alleged accounts of the quantum theory which never mention the name of Jeans, or of other workers in this country, except in purely subsidiary ways.

Sommerfeld's brilliant generalization—and to a less extent even Bohr's angular momentum principle—were anticipated in this country by authors who receive little, if any, mention in current accounts. This detracts not at all from the brilliant nature of the work described; but Dr. Jeans is scrupulously fair, except perhaps to himself.

This may sound controversial, but not against the author. It is in some ways a protest, growing daily more insistent among workers, against the logical nature of present physical deductions. Physics will not advance by the persistency of advocates who either slur over or ignore difficulties, and refuse to even see phenomena which do not fit into a preconceived view of atomic structure and the relation of the quantum theory to it. The present Report is not open to this objection. From end to end, the author deals with every problem on its merits, and keeps an open mind in cases of doubt, but omitting nothing which is relevant, either in experimental research or in theoretical dynamics. In this respect, his account is unique, and of a value which it is difficult to estimate.

The reviewer is writing as one who believes in the fundamental validity of the quantum theory in certain respects—as one who believes in the views laid down by Bohr, but not the vague analogies of Bohr's followers, which are opposed to the logical nature of Prof. Bohr's own writings, which should be taken as a model. If we may take a particular case, pointed out already by others, Bohr's correspondence principle is a definite mathematical thing, whose application is precisely defined. But in the hands of his followers strange things are deduced from it, by analogies which entirely obliterate its real significance and value, and cannot, in fact, be logically connected with it. At this point we end a plea that the writings of Dr. Bohr be taken as the standard—Dr. Jeans has so taken them. The result is that his short discussion of the correspondence principle may disappoint many readers who wish to get ahead; but it is fair and final, and contains all that can really be deduced. Perhaps this review goes too much into detail on general principles. Yet such general principles are always present to those who really see the development of the quantum theory in a logical manner. Unfortunately, they do not include many of our experimental physicists. But they do include Prof. Bohr himself and the author of this Report.

The "adiabatic invariants" of Prof. P. Ehrenfest constitute, perhaps, the most beautiful sign of any hope of reconciling the quantum theory with the older dynamics. The author gives due space to this investigation.

We can only say, in conclusion, that the first fair picture of the present state of the quantum theory has been given—just as the first edition of this Report gave it so soon after the initial formulation of the quantum theory. The work before us is quite necessary to any library of modern physics.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[SIXTH SERIES.]

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AUGUST 1924.

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XXVII. *On the Strength of Tungsten Single Crystals and its Variation with Temperature.* By The Research Staff of the General Electric Co., Ltd.\* (*Work conducted by F. S. GOTCHER.*)

[Plates VI.-VIII.]

*Summary.*

By heating drawn tungsten wires to a high temperature, large crystals are developed with random orientation of crystal axes, many of which occupy locally the complete volume of the wire. If these wires are subjected to a suitable tensile stress, some of these large crystals will deform by a process of slip; and one will eventually fracture. The orientation of the crystal axis in this crystal is such that two sets of slip planes are symmetrically inclined to the direction of stress, and the crystal fractures in the form of a wedge symmetrical to the stress. This affords a very simple means of studying the deformation of single crystals under conditions involving a minimum distortion of the crystal lattice.

Measurements are made on the strength of such crystals in wires of various diameters and at temperatures varying from 700° K. to the melting-point. It was found that the time required for fracture—which may be regarded as an inverse measure of the mean rate of deformation—is approximately an exponential function of the load and the temperature; that for a given rate of deformation the load is proportional to the cross-sectional area; and—apart from transition temperatures—is a linear function of the temperature.

\* Communicated by the Director.

*Phil. Mag.* S. 6. Vol. 48. No. 284. Aug. 1924.

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Discontinuities occur in the load-temperature curves at temperatures approximately  $850^{\circ}$ ,  $1600^{\circ}$ , and  $2600^{\circ}$  K. Variations in other physical properties are found to occur at the same temperatures, which leads to the view that these changes represent "transformation points" of a new type. Some new measurements on the thermal expansion of tungsten are recorded.

### (1) *Introduction.*

THE deformation of single metallic crystals under stress has been studied by G. I. Taylor and C. F. Elam \* working with aluminium, and by Polanyi and his collaborators working with zinc † and tin ‡. It has been established for all these metals that deformation takes place by slip on certain crystal planes characteristic of the metal, and that this usually results in a re-orientation of the crystal axis. In the case of aluminium it was shown that the crystal tended to assume an orientation such that two sets of slip planes were symmetrical with the direction of stress; and it appeared probable that there would be an equal amount of slipping on these two sets of planes near the point of fracture if this condition were completely realized: in this case the fracture would be a wedge symmetrical to the stress.

But no systematic study appears to have been undertaken on the strength of these crystals, taking into account the relation between the rate of deformation on the one hand, and the load, temperature, and orientation of the crystal planes on the other. Such a study would be very difficult if ingots composed of a single crystal were used; for in such ingots there is no constant relation between the direction of the crystal axis—before deformation—and the external form of the ingot; which no doubt accounts for the wide variation of tensile strength observed in such ingots §. This difficulty might be overcome by the use of long fine wires made up of many crystals oriented in all directions, of which a considerable number occupy locally the complete volume of the wire. In such a wire chance would insure that at least one of them would be oriented relative to the axis of the wire very nearly in the direction most favourable to slip under stress applied along the wire. If the wire is stretched, slip should occur most easily in that crystal which has the most

\* G. I. Taylor and C. F. Elam, Roy. Soc. Proc. A, vol. cii. p. 643 (1923).

† Mark, Polanyi, and Schmid, *Zeit. f. Phys.* xii. (1922).

‡ Mark and Polanyi, *Zeit. f. Phys.* xviii. pp. 75-96 (1923).

§ H. C. H. Carpenter and C. F. Elam, Roy. Soc. Proc. A, vol. c. p. 329 (1922).

favourable orientation; and if the wire is broken, the fracture should occur by a division of this crystal into two wedges symmetrical to the direction of stress, with re-orientation of the crystal axis. Our experiments show that these conditions can be realized in tungsten wires which have been given a suitable heat treatment, if wires 10 cm. long and less than 0.20 mm. diameter are used. Further, tungsten is a suitable metal for such investigations, because it can be obtained exceptionally pure, and the conditions of crystal growth can be so regulated that the crystals are very uniform.

## (2) *Material Employed.*

The tungsten wires employed in the investigation were made by the usual process of reducing the oxide in hydrogen, and pressing, "forming," swaging, and drawing the resulting metal. The oxide employed was prepared with all possible precautions for purity; most of the impurities left were removed during "forming," that is to say, heating the pressed bar to a temperature in the neighbourhood of its melting-point. Ordinarily a forming temperature just under 3000°K is employed, but in the case of most of the wires studied a temperature somewhat above 3000° K. was used. As a result of this treatment, and of that involved in growing comparatively large crystals in the wire, the residual impurity was reduced below 0.01 per cent.

The drawn wire is, of course, fibrous; but if this wire is heated for a few minutes to a temperature about 3000° K., "Recrystallization" takes place, with a random orientation of crystal axes, and rapid crystal growth occurs with the result that many of the crystals fill the whole cross-section of the wire. This treatment was applied to all wires used in these experiments before the measurements were made, and no material was accepted which did not show a reasonably symmetrical wedge-shaped fracture, characteristic of single crystals in the most favourable orientation.

Photographs 1, 2, 3 (Pl. VI.) show such fractures. 1 is a perspective view of a wedge, the outline of the crystals being revealed by etching; 2, 3 show views of another wedge in perpendicular directions. The partially-formed wedge should be noted; it is markedly asymmetrical, as compared with the almost perfect symmetry of the wedge at which fracture has occurred; but in both wedges, the reduction of area has occurred in one plane only. Figs. 4, 5, and 6 (Pl. VII.) show sections through wires, etched to show the crystal structure. Fig. 4 shows a wedge fracture in a single crystal. Fig. 5

shows a partially-formed wedge in one of the smaller wires, the deformed part being again a single crystal; the neighbouring crystals are not deformed. Fig. 6 is a section of the thickest wire used (0.195 mm. diameter); it shows that even in this wire, crystals occupying the full cross-section of the wire are obtained, and that deformation—asymmetrical in this case—is confined within the limits of such a large crystal. These photographs provide sufficient evidence that the fractures studied are, like those of aluminium, true single crystal fractures; and that approximately symmetrical wedges are formed at fracture.

Sykes\* has previously observed similar wedge-shaped fractures in molybdenum wires, and Jeffries and Archer†, before Taylor and Elam's work was published, suggested that such wedges might have been caused by slip on conjugate planes inclined at  $45^\circ$  to the axis of the wire.

### (3) *Deformation of Tungsten Crystals.*

X-ray analysis was used to determine the nature of the deformation produced in the fractured crystals. A spectrometer of the photographic type was employed, using Cu K $\alpha$  radiation; the constants of the spectrometer were determined by means of a crystal of rock-salt. Since the crystal structure of tungsten is known‡, the reflecting planes could be identified by the position of the reflexions on the photograph.

Figs. 7–11 (Pl. VIII.) show such photographs. Fig. 7 was taken with a thoroughly annealed fine tungsten wire—composed of many small crystals oriented at random—rotating at the spectrometer axis parallel with the X-ray beam. The wire did not extend fully across the beam, and consequently lines appear only in the upper half of the photographs. The lines shown are those corresponding to the (110), (100), and (112) planes.

Reflexions from individual crystals, in particular those forming wedges, were obtained by mounting the wires in hard glass and cutting sections through them in such a way that the surface of the crystal to be examined alone was exposed. The surfaces were polished and etched, and the reflecting planes most nearly inclined to these sections gave intense lines, which were as sharp as those obtained from uncut crystal. Fig. 8 shows the reflexion obtained from a section perpendicular to the axis of the wire through the crystal

\* W. P. Sykes, *Am. Inst. Mining Eng. Trans.* Feb. 1921.

† Z. Jeffries and R. S. Archer, *Chem. & Met. Eng.* xxvii. p. 751 (1922).

‡ P. Debye, *Phys. Zeit.* xviii. p. 483 (1917).

forming a wedge; many such photographs, taken from sections cut through different positions of wedges, and from wedges formed at different temperatures, establish the fact that the crystal forming the wedge has its (110) plane perpendicular to the axis of the wire within about  $10^\circ$  in all cases. In fig. 9 the reflexion was from a section parallel to the edge of the wedge and inclined to the axis of the wire; the (112) plane is indicated. Fig. 10 shows a reflexion from a section inclined to the axis of the wire, but perpendicular to the plane containing the wedge edge and the wire axis; it shows a (100) reflexion. These reflexions are consistent with a single crystal formation. It is to be noted, however, that the lines in figs. 9 and 10 are not sharp, but are drawn out in a direction parallel to the spectrometer slit, which indicates a slight curvature in the crystal planes.

This analysis shows, therefore, that deformation has not been accompanied by any break-up of the crystal or any marked re-orientation of the crystal axis. It must therefore have occurred as the result of slip along definite crystal planes, and the planes of slip must be of the form (11*n*). The (112) planes are the most probable, having the widest spacing and the densest packing of atoms; the full evidence that they are indeed the slip planes will be given in a later paper. It is remarkable that the (112) planes rather than the (100) are the planes of slip, for the (100) were found to be the cleavage planes.

It is of interest to note that the particular orientation of the crystal axis with respect to the wire axis in the case of the crystals which fracture is that found by Burger\* to predominate in drawn tungsten wire, although the wire was drawn from a crystal aggregate with random orientation of crystal axes. Our experiments show that with this orientation the crystal is stable, and they yield the additional information that under these conditions the crystal offers minimum resistance to symmetrical extension by a process of slip.

The measurements about to be described on the laws of flow of these crystals may therefore be considered as applying to that condition of the crystal which most frequently occurs in the crystal aggregate when deformed under drawing stresses.

#### (4) *The Mechanism of Deformation.*

We reserve fuller discussion of the formation of the wedge to a later paper, but certain conclusions with regard to this are of importance in connexion with the interpretation of

\* H. C. Burger, *Phys. Zeit.* xxiii. p. 141 (1922).

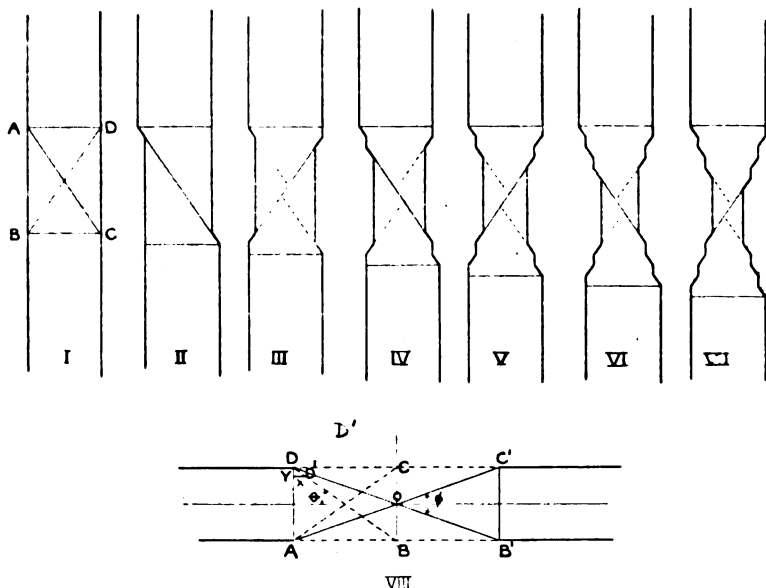


the measurements to be described. These have to do with the time required for fracture and the extension of the crystal during fracture.

The manner of formation of these symmetrical wedges must be that suggested by Jeffries and Archer, except that in this case the slip planes are not inclined at an angle of  $45^\circ$  to the direction of stress, as he supposed, but at the more oblique angle of  $35^\circ 15'$ . They assumed a succession of slips on alternate conjugate slip planes, which results in an extension of the crystal and at the same time a reduction of the diameter in a plane perpendicular to the two sets of slip planes. The reasons for this alteration of slip need not concern us here.

Such a process is illustrated by the diagrams I–VII (fig. 1),

Fig. 1.



which represent successive stages of deformation of a crystal in a test curve. These diagrams are similar to those given by Jeffries and Archer. ABCD (No. I) represents a section of a crystal cut parallel to the wire axis, AC and DB being the directions of the two sets of slip planes. Nos. II–VII show a succession of slips which result in a progressive extension of the crystal and at the same time a progressive reduction of the diameter in the plane of the section. If the slips are small in comparison with the dimensions of the crystal, and if there is on the average just as much slipping

on one set of planes as on the other, a completely symmetrical fracture may be produced. Without making any assumptions as to the extent of slipping on any one plane or as to the numbers of slips required for fracture, it follows that the extension of the crystal is a function of the angle made by the slip planes with the direction of the wire axis and the diameter of the crystal before deformation.

Consider the diagram No. VIII. Let ABCD represent the crystal before deformation and DOA and C'OB' two parts of the divided crystal just after fracture. Let DB and AC represent the directions of the slip planes which make an angle  $\theta$  with the direction of the wire axis. Then any small slip DD' along DB may be represented as an extension  $x$  in the direction of the wire axis, and as reduction of diameter  $y$  perpendicular to the wire axis where

$$y = x \tan \theta.$$

If we consider the fractured crystal as having been produced by the summation of a larger number of such slips parallel to DB or parallel to AC, then the total extension BB' will be given by

$$BB' = \Sigma x = \Sigma y \cot \theta.$$

But  $\Sigma y$  is equal to AD when fracture occurs, so that

$$BB' = AD \cot \theta.$$

$$\text{For the value } \theta = 35^\circ 15',$$

$$BB' = 1.41 \text{ AD.}$$

It may be pointed out that the angle  $\phi$  of the symmetrical wedge formed by such an extension will be given by

$$\phi = 2 \tan^{-1} \left( \frac{1}{2} \tan \theta \right),$$

$$\text{which, if } \theta = 35^\circ 15',$$

$$\text{gives } \phi = 38^\circ 56'.$$

Many crystal wedges formed by fracture of the test wires had angles agreeing with this value within one or two degrees. Such a wedge is that shown in photo No. 4 (Pl. VII.).

A large number of wedges had angles larger than this value, but the results of experiments to be described in a later paper showed that the slip planes were the same as in the case of the narrow wedges, though the relative amount of slipping on the two sets of slip planes was not the same, owing to a slight asymmetry in the inclination of the crystal axis with respect to the direction of stress. This slight asymmetry would not, however, appreciably effect the total amount of extension required for fracture.

Assuming that the mechanism of fracture is substantially that described, it is clear that the time required for fracture serves as a measure of the mean rate of slip or extension within the crystal which fractures; and that in studying the conditions for fracture the time for which the load is applied is quite as important as the load or the temperature.

Doubtless, owing to the progressive reduction in area of the slip planes, the rate of extension will increase rapidly near the point of fracture; and if distortion of the slip planes occurs the rate of extension will be altered. But it may be safely assumed, however, that crystals of equal diameter which deform into similar wedges on fracture will deform at the same mean rate if the time required for fracture is the same.

#### (5) *Apparatus.*

In studying the strength of these crystals, a measured tension was applied to the wire electrically heated in vacuo, and the time for fracture noted. The temperature was determined by using the well-established relations of Langmuir\* between current and temperature.

The apparatus consisted of a tungsten and steel buoy floated in mercury, and attached to the lower end of the wire, the upper end of which was fixed. The amount of tension could be regulated by depressing the mercury level below the floating-point of the buoy by means of a mercury column controlled from outside the vacuum; the control included a slow-motion device.

Fig. 2 gives a diagrammatic view of the experimental arrangement. The wire *W* is attached at its upper end by means of a clamp *C*<sub>1</sub> to a removable stopper *J*, which can be sealed with mercury into the containing vessel. At its lower end the wire is attached by means of a clamp *C*<sub>2</sub> to the tungsten and steel buoy *R*<sub>1</sub> *S* *R*<sub>2</sub> *T*, which is constructed as shown. *T* is a heavy mass of tungsten; *S* is a steel cylinder; *R*<sub>1</sub> and *R*<sub>2</sub> are supporting rods of small diameter which serve to space the steel and tungsten so that the centre of gravity of the system is low. They also pass freely through two holes in the guide-piece *G*, which is necessary to keep the buoy from touching the sides of the glass vessel. *G* is so constructed that it lightly grips the sides of the glass vessel when the wire, with buoy attached, is lowered into position, and it may be removed with the buoy. *B* is a section of rubber tube fastened to the glass vessel so as to act as a buffer for the falling buoy when the wire breaks.

\* I. Langmuir, *Phys. Rev.* vii. p. 302 (1916).

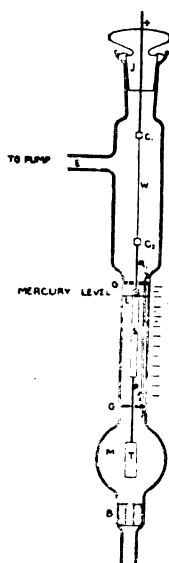
If the friction is negligible, the tension  $T$  will be given by

$$T = \frac{\pi D^2 \rho h}{4},$$

where  $D$  is the diameter of  $S$ ;  $\rho$  the density of mercury; and  $h$  the displacement of the mercury level from the floating-point.

Calibration of the buoy could be carried out by attaching the upper end to a beam balance in the open air and varying the mercury level, the whole operation being carried out with the buoy in position in the glass containing vessel.

Fig. 2.



Such a calibration showed that the friction forces could be neglected and that the calibrated value could be used. A wide range of tensions varying from a fraction of a gram to several hundred times that value could be covered by the use of a few buoys of different sizes.

The wire was heated electrically through the lead to  $C_2$  sealed into the glass stopper  $J$ , and by means of the mercury. The current was measured on a standard Weston Ammeter.

The pumping system was such that a pressure less than 0.001 mm. Hg. could be attained in a few minutes, and liquid air was used near the containing vessel. Under these conditions the current temperature relations accurately applied.

(6) *Method of Measurement.*

As it was necessary to give the wires a preliminary heat treatment in order to develop a suitable crystal structure before applying the tension, the procedure adopted was as follows:—

- (1) The wire in the hard-drawn state was clamped between  $C_1$  and  $C_2$  outside the containing vessel, and the whole was lowered into position in the vessel and J sealed with mercury; the total weight of the buoy is easily sustained by the wire in the drawn state.
- (2) The vessel was exhausted and the mercury level brought to the floating-point marked on the buoy, so that the wire was put into a condition of no tension.
- (3) The wire was given its preliminary heat treatment; at the same time it was straightened by means of a very slight tension, which was less than that required to stretch the wire.
- (4) The tensile test was carried out by applying the tension to the wire when cold, then heating the wire to the desired temperature and observing the time required for fracture. As the wire always extended during fracture, the level of the mercury was kept a constant distance below the floating-point by depressing the mercury level at a rate equal to that at which the wire extended.

(7) *Experimental Results.*

Measurements were carried out on these test wires under a wide variety of conditions of wire diameter, temperature, load, and time required for fracture. It was found that symmetrical wedge-shaped fractures of the same type occurred at all temperatures between  $700^\circ \text{K.}$  and the melting-point; and that the time required for fracture under given conditions of load and temperature could be varied at will from a few seconds up to an indefinite time. As the observations became more variable as the time was increased, ten minutes was adopted as the upper limit in the case of the measurements described. In every case the time ( $t$ ) required for a load ( $L$ ) to break a wire of cross-sectional area ( $\sigma$ ) at a temperature ( $T$ ) was observed directly. But by a suitable combination of the observations the following relations which are specially important can be deduced:—

- (1)  $L, t$  variable ;  $\sigma, T$  constant.
- (2)  $L, \sigma$     „     $t, T$     „
- (3)  $t, T$     „     $L, \sigma$     „
- (4)  $L, T$     „     $\sigma, t$     „

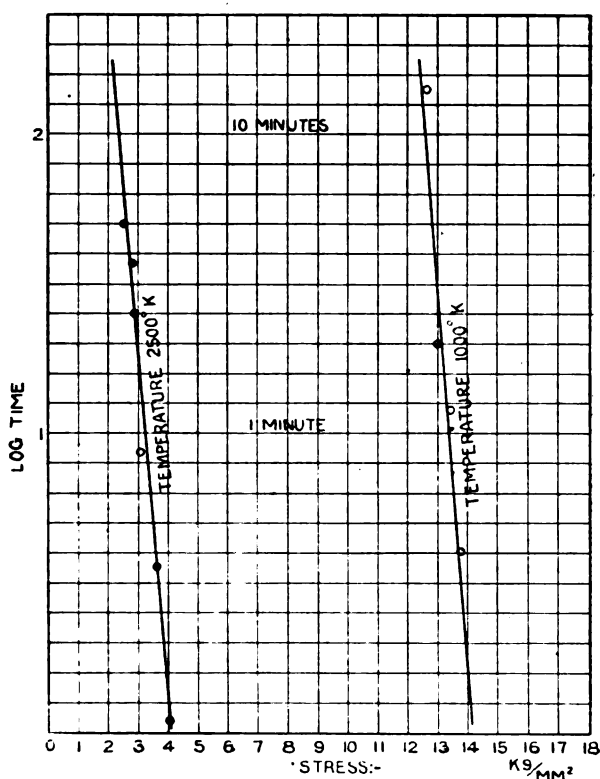
As the relations deduced are derived from the same observations, they are inevitably consistent with each other.

(8) *The Relation between Time and Load.*

Though the time to fracture varies very rapidly with load, measurements could be obtained which clearly showed the law governing this change for a range of time varying from a few seconds up to ten minutes or more.

Typical time-load curves are shown in fig. 3, in which the

Fig. 3.

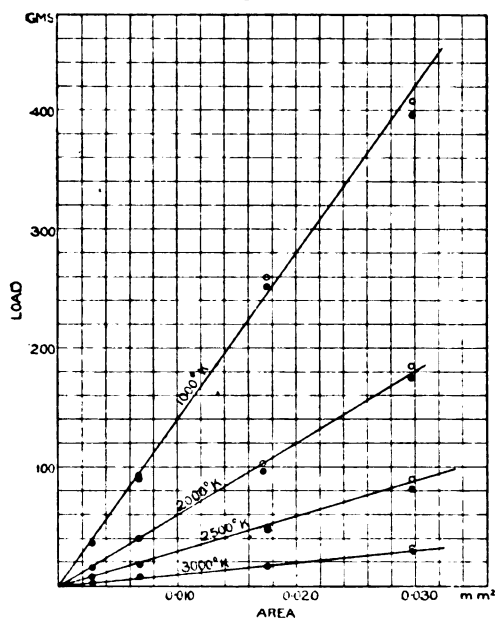


logarithm of the time in minutes is plotted against  $L/\sigma$  expressed in  $\text{kg./mm.}^2$ . Two curves are shown—one for a temperature of  $2500^\circ\text{K.}$ , and one for a temperature  $1000^\circ\text{K.}$  The test-wires were of a diameter  $0.093\text{ mm.}$ , the preliminary heat treatment being  $3100^\circ\text{K.}$  for two and a half minutes. Similar curves were obtained for wires of other diameters, the slope being approximately the same in all cases.

(9) *The Relation between Load and Cross-sectional Area of the Test-wire.*

By taking a sufficient number of time-load curves for wires of different diameters, at the same temperature, the load required to fracture such wires could be obtained as a function of the cross-sectional area of the test-wire for any arbitrary value of time. If equal mean rates of deformation are required, the times must be chosen as proportional to the wire diameter; but as the time to fracture varies rapidly with the load, a comparison on the basis of equal times would introduce relatively small errors.

Fig. 4.

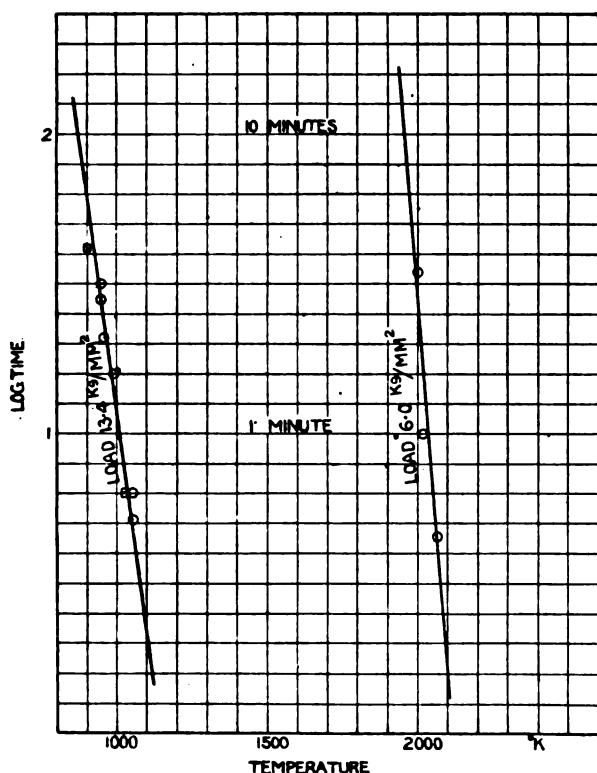


Curves (fig. 4)—points marked—summarize the measurements made in this way; the load in grammes required to fracture the wire is plotted against the cross-sectional area of the wire in  $\text{mm}^2$ . The black circles represent values of load for time chosen proportional to the diameter, that for the smallest wire being one minute; the open circles represent values for equal times, viz. one minute. The wires varied in cross-sectional area from  $0.0028 \text{ mm}^2$  for wires  $0.06 \text{ mm}$ . in diameter to  $0.0297 \text{ mm}^2$  for wires  $0.195 \text{ mm}$ . in diameter. The preliminary heat treatments varied from  $2900^\circ \text{K}$ . for 1 minute in the case of the smallest wire to  $3100^\circ \text{K}$ . for  $2\frac{1}{2}$  minutes for the largest. The observations

were made at four different temperatures, viz.  $1000^{\circ}$ ,  $2000^{\circ}$ ,  $2500^{\circ}$ , and  $5000^{\circ}$  K.

It is clear that the variations in the strength of the crystals from wire to wire are greater than the differences introduced by this change in the ratio of times. We may consider, however, that within the limits of experimental error the load required to fracture these crystals at a constant rate of

Fig. 5.



deformation and at the same temperature is proportional to the cross-sectional area of the crystal before deformation, over a wide range of the variables.

#### (10) *The Relation between Time and Temperature.*

The curves of fig. 5 show the relation between temperature and the time required for a given load to fracture the wire; the logarithm of the time is plotted against the temperature. Curves for two different loads are shown, viz.  $13.4 \text{ kg./mm.}^2$  and  $16.0 \text{ kg./mm.}^2$ ; the test-wires were  $0.093 \text{ mm.}$  in diameter.



the preliminary heat treatment was  $3100^{\circ}$  K. for  $1\frac{1}{2}$  minutes. The experiments are not capable of great accuracy because the time varies so rapidly with the temperature; but they are sufficient to show that the observations tend to lie on straight lines. Consecutive portions of the test-wires naturally gave the most consistent results. Very large numbers of curves of this same type were obtained with all wires and for all values of load which fractured these wires in measurable times at temperatures ranging from  $700^{\circ}$  C. to very near the melting-point.

Some observations were also made by another method. The squares plotted on the curve for the load  $13\cdot4$  kg./mm.<sup>2</sup> were obtained by heating the test-wires in an electric furnace—within the vacuum,—the temperature being obtained by means of a calibrated thermo-couple of nickel-nichrome. This was done as a check on the method of heating. The results of the two methods agree within the limits of experimental error.

#### (11) *Relation between Load and Temperature.*

The consistency of the observations relating to time required for fracture and temperature makes it possible to determine the temperature for a given time and for a given load to within  $50^{\circ}$  on our temperature scale.

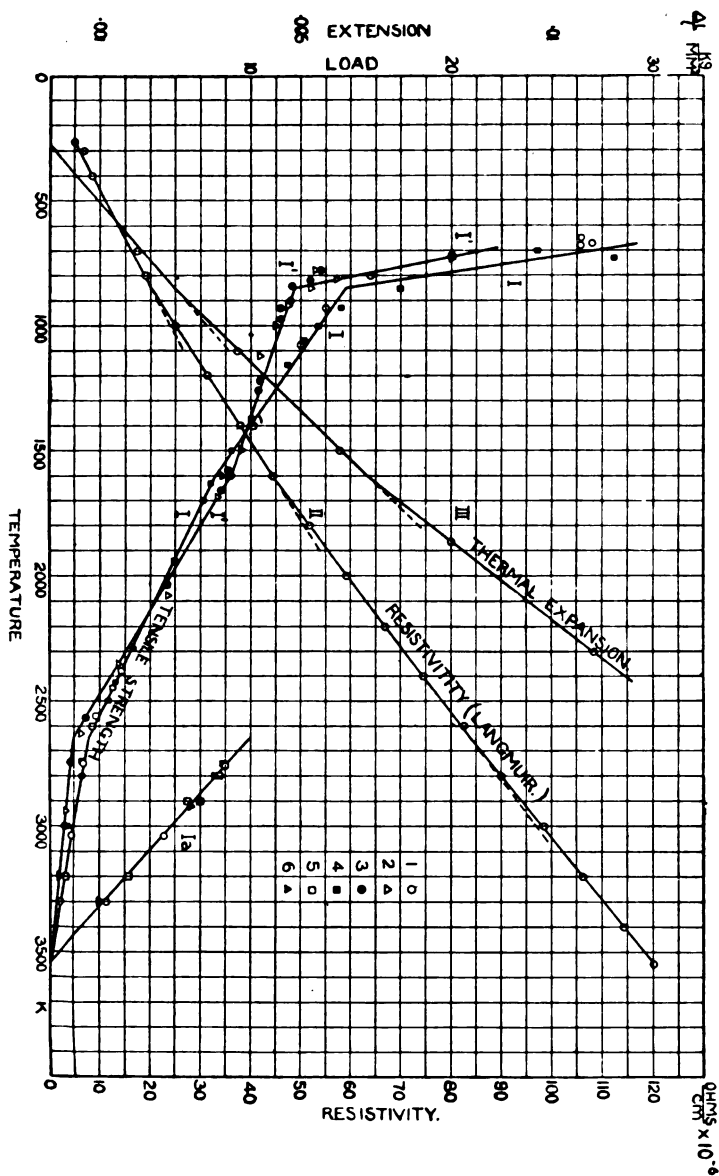
By making a sufficient number of observations relating time and temperature for a given load, so that the temperature corresponding to the one minute value of time could be estimated, the relation between load and temperature was obtained at various temperatures from  $700^{\circ}$  K. to within a few hundred degrees of the melting-point for a variety of wires of different diameters.

Curves I, I<sup>1</sup>, and I<sup>a</sup> (fig. 6) summarize the results of such measurements. The load in kg./mm.<sup>2</sup> is plotted against absolute temperature.

The wires used were of different diameters, and were drawn from ingots formed at two different temperatures. The following table gives the key to the observations as plotted in the curves (fig. 6):—

Wire number.	Diameter mm.	Forming temperature.	Preliminary heat treatment.
1 .....	0.06	above $3000^{\circ}$	$2900^{\circ}$ for 1 minute.
2 .....	0.05		" " "
3 .....	0.06	below $3000^{\circ}$	" " "
4 .....	0.093	above $3000^{\circ}$	$3100^{\circ}$ for $1\frac{1}{2}$ "
5 .....	0.195	" "	" <sup>21</sup> / <sub>2</sub> "
6 .....	0.10	" "	$2900^{\circ}$ " 2 "

Fig. 6.



Curve I *a* is merely the portion of Curve I above  $2700^{\circ}$  K. plotted on a magnified scale. Most of the fractures obtained below  $800^{\circ}$  were probably intercrystalline; a symmetrical wedge was not formed at the fractured end. In this case, however, the crystal was stronger than the crystal boundaries; the observations thus have some significance from the point of view of strength, so some of these are plotted. The crossed circle at  $700^{\circ}$  K. represents observations made with wires which did form wedges on fracture.

The most remarkable feature of these results is the presence of sharp changes in the load-temperature curves which indicate definite discontinuities. These discontinuities, which are characteristic of each of the wires used, occur at temperatures between  $800^{\circ}$ – $900^{\circ}$  K., at about  $1600^{\circ}$  K., and again at  $2600^{\circ}$ – $2700^{\circ}$  K. The observations appear to lie on straight lines between these regions of sharp changes, and for this reason these lines have been drawn through the observed points to intersect at these transition temperatures. It is noteworthy that the straight line above  $2700^{\circ}$  K.—plotted on the magnified scale in I *a*—appears to cut the temperature axis at a temperature very close to the melting-point, given by Langmuir as about  $3570^{\circ}$  K.\*

But the observations are not wholly consistent; they divide themselves into two distinct groups, which differ particularly in the slopes of the curves on either side of the  $1600^{\circ}$  K. discontinuity. The division cannot be due to differences of purity which might arise from differences in forming temperature; for though Group II includes the only wire formed at the lower temperature, it includes also the 0.05-mm. wire, which is of the same material as those in Group I and merely drawn to a smaller diameter. Neither can the differences be accounted for by the preliminary heat treatment, as the 0.06-mm. wires in Group I were given the same treatment exactly as those in Group I<sup>1</sup>.

The wires falling in Group I<sup>1</sup> appear to give the most consistent results and the sharpest discontinuities. It is possible that this is connected with the previous history of the wires, for although every effort was made to give the same mechanical treatment, variation in die steps and temperatures from wire to wire are unavoidable. Such differences may modify the crystal structure in some way which affects the strength. A further study of the physical properties of these wires may throw more light on this point.

\* I. Langmuir, *Phys. Rev.* vii. p. 302 (1916).

(12) *Variation of other Physical Properties with Temperature.*

The discovery of discontinuities in the relation between load and temperature suggest that existing data on the variation of other physical properties with the temperature should be examined to see if they indicate the presence of such discontinuities.

Curve II (fig. 6) shows Langmuir's values for electrical resistivity\* plotted against temperature. Clearly the observed points are consistent with discontinuities at the same transition temperatures as those shown by the strength curves, though the changes are too small to locate these temperatures with any accuracy. The circles (Curve III) show some of Worthing's† observed points for thermal expansion plotted on the same temperature scale. These show changes which are certainly consistent with a discontinuity at about  $1600^{\circ}$  K., but there are not enough observations to show the presence of any discontinuity at lower temperatures. His results point to a change in expansion coefficient somewhere between room temperatures and  $1300^{\circ}$  K., but he represents the change as gradual.

These results appear to support the existence of these transition temperatures, but it seemed especially desirable to supplement Worthing's measurements on thermal expansion, in particular at low temperatures.

(13) *Thermal Expansion Measurements.*

The apparatus used for the tensile strength measurements was well suited for the measurements of expansion of these wires at high temperatures; it was only necessary to observe the extension of the lower end of the wire with a cathetometer when just sufficient tension was applied to the wire to keep it straight, but not enough to give it a permanent extension. The temperatures were measured by the heating current, the error due to the cooling at the ends of the filament being eliminated by measuring the extension for two different lengths of the filament and taking the difference in the extensions at corresponding temperatures.

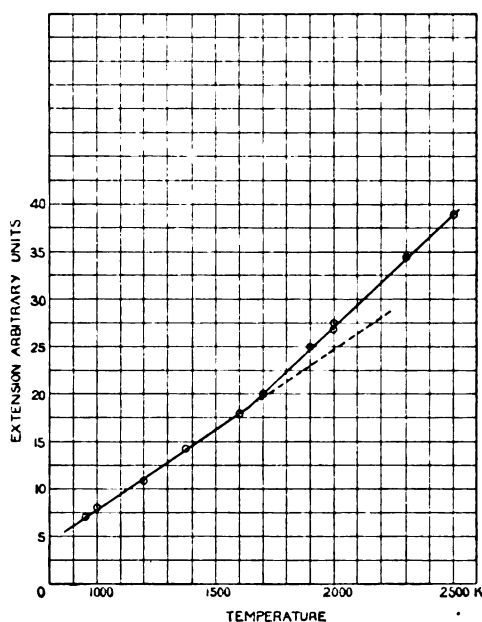
Fig. 7 shows a typical extension-temperature curve obtained with a wire 12 cm. in length. The extension is plotted in arbitrary units. The observations clearly lie on straight lines, above and below a temperature between  $1600^{\circ}$  K.

\* I. Langmuir, *Phys. Rev.* vii. p. 154 (1916).

† A. G. Worthing, *Phys. Rev.* x. p. 638 (1917).

and  $1700^{\circ}\text{K}$ . A similar curve was obtained for a wire 24 cm. in length, and the slope of the difference curve yielded values of the coefficient of expansion which agreed well with Worthing's values, especially above the transition temperature. Observations of this type were made on wires of three different diameters: all agreed in giving a transition temperature of about  $1650^{\circ}$ , and the coefficients of expansion calculated were  $7.34$ ,  $7.17$ , and  $7.30 \times 10^{-6}$  respectively above the transition temperature and  $5.80$ ,  $5.30$ , and  $6.0 \times 10^{-6}$  below the transition temperature. The mean of the higher value,  $7.27 \times 10^{-6}$ , agreed very well with Worthing's value

Fig. 7.

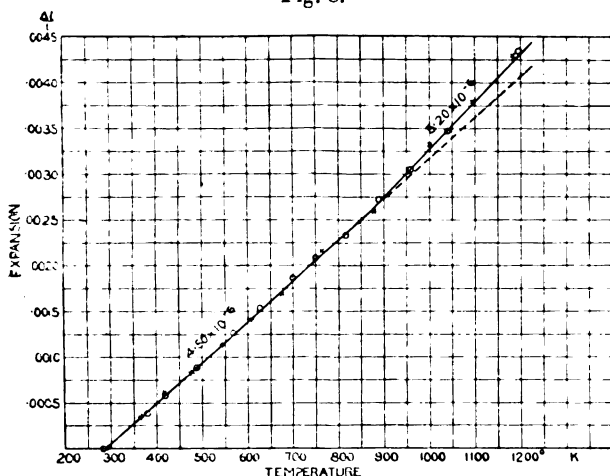


$7.26 \times 10^{-6}$  for the temperature  $2300^{\circ}\text{K}$ ., that of the lower value  $5.71 \times 10^{-6}$  being somewhat high as compared with Worthing's value  $5.19 \times 10^{-6}$  for temperature  $1300^{\circ}\text{K}$ . The higher values were considered much more reliable, as the measured extensions were so much larger, and the wires were no doubt straighter at the higher temperatures. There is no doubt, however, about the sharpness of the discontinuity under these experimental conditions. It is to be noted that

the measurements were made under conditions of slight tension.

In order to investigate the expansion at lower temperatures a different method was employed. The expansion of a tungsten rod 1 mm. in diameter was measured by comparing its expansion with that of silica in an electric furnace, the temperature of which was measured by means of a platinum-rhodium thermo-couple. The first measurements on this tungsten rod did not indicate any sharp discontinuity at the temperature expected, but by annealing it very near its melting-point consistent results were obtained which clearly revealed a discontinuity. The results of these measurements are summarized in curve (fig 8), in which the observed points

Fig. 8.



represent two sets of readings. They clearly show that a sharp discontinuity in the expansion curve exists at about  $850^{\circ}\text{K}$ ., which is in good agreement with the transition temperature indicated by the tensile-strength measurements. Here, again, the coefficients of expansion are constant above and below that temperature. The value below  $850^{\circ}\text{K}$ . was  $4.50 \times 10^{-6}$  as compared with Worthing's value of  $4.44 \times 10^{-6}$  for room temperatures; above  $850^{\circ}\text{K}$ . the value was  $5.20 \times 10^{-6}$ , which is in excellent agreement with Worthing's value for  $1300^{\circ}\text{K}$ .: it therefore appears most probable that this value holds up to  $1600^{\circ}\text{K}$ . It is to be noted that these measurements were made under conditions which put the specimen under very slight compression.

Fig. 6 (Curve III) summarizes in heavy line the results of the thermal expansion measurements, Worthing's values being represented by the circles. Clearly our measurements are not inconsistent with his, but they go further in that they reveal the constancy of the coefficients apart from these transition temperatures.

The measurements were not carried out above  $2600^{\circ}$  K. so that no check was obtained on the  $2600^{\circ}$  K. discontinuity found in the case of the tensile-strength curves.

#### (14) *Discussion.*

The chief results of our experiments are those which concern, first, the relations between the variables affecting deformation, second, the existence of transition temperatures for the physical properties of tungsten.

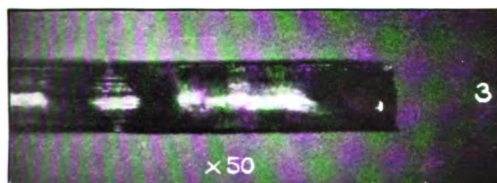
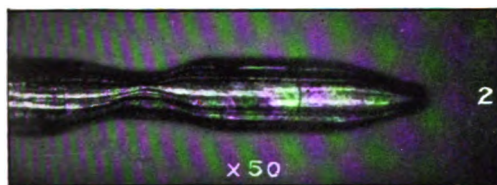
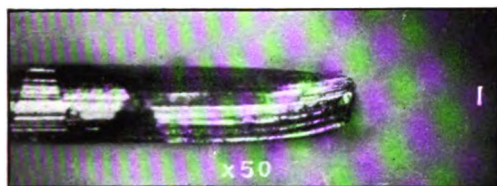
We find that the time of fracture which we regard as an inverse measure of the mean rate of deformation is approximately an exponential function of the load and the temperature. For a given mean rate of deformation the load is proportional to the cross-sectional area and, between transition temperatures, is a linear function of the temperature.

The only experiments on single crystals with which we can compare our own are those of Schönborn\*, who also found that the rate of deformation was an exponential function of the load. His absolute values varied from specimen to specimen, doubtless because he did not secure a constant relation of crystal axis to direction of stress. But some of our relations accord well with those found in crystal aggregates, and suggest accordingly that the laws governing the deformation of such an aggregate are intimately connected with those governing the deformations of the individual crystals. Thus it is known that for such aggregates the rate of extension varies very rapidly with load and temperature. Further, Andrade† in his study of the viscous flow of metal aggregates found that, for a constant rate of flow, the load was proportional to the cross-section. Again, the rate of flow in liquid viscosity is approximately an exponential function of the temperature. Lastly, Jeffries and Archer's‡ results on the variation with temperature of the tensile strength of

\* H. Schönborn, *Zeit. f. Phys.* viii. p. 377 (1921).

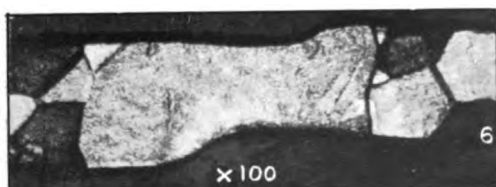
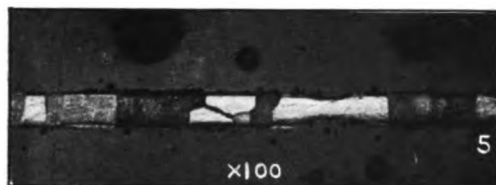
† E. N. da C. Andrade, *Roy. Soc. Proc. A*, vol. xc. p. 329 (1914).

‡ Z. Jeffries and R. S. Archer, *Chem. & Met. Eng.* xxvii. p. 8s2 (1922).

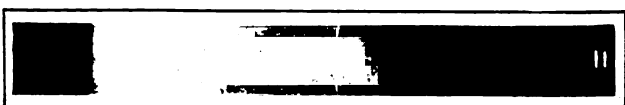
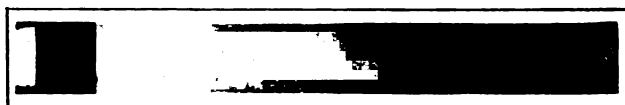
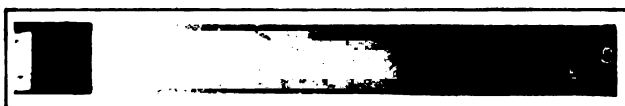
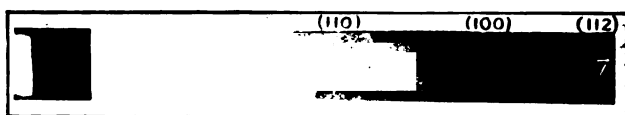














tungsten agree well with our relation between load for a given rate of deformation and temperature. The multi-crystal wire used by them is many times stronger than our single crystals, but curves of much the same shape are obtained for temperatures ranging from  $300^{\circ}$  to  $1200^{\circ}$  K.; in particular they found a change in strength occurring at about  $800^{\circ}$  K. The comparison cannot be carried to higher temperature because crystal growth affects the results.

The explanation of all these relations doubtless awaits further measurement and the development of the theory of crystal structure. It is to be hoped that this method of measurement, which has yielded such definite results in the case of tungsten, can be applied to other metals.

The significance of the transition temperatures and the nature of the changes which cause the alteration of physical properties at these temperatures are very obscure. Ordinary "transformation points" in metals are usually associated with some re-arrangements of the atoms indicated by a change in the crystal structure of the material. But direct investigation has shown that between room temperature and  $2000^{\circ}$  K. the crystal structure of tungsten undergoes no change other than that due to mere expansion. Fig. 11 (Pl. VIII.) shows on the same film two X-ray spectra given by the same tungsten wire, one with the wire at room temperature, the other with the wire heated to about  $2000^{\circ}$  K.; the displacement of the lines at the higher temperatures is just that expected on the ground of expansion.

Perhaps the variation in the nature of the change at the transition temperature, which is indicated by the two curves in fig. 6, may provide the clue. If it can be found why two wires, though showing discontinuities at the same temperature, show different discontinuities, much light will be thrown on the problem. Work is proceeding in this direction; for the time being we would merely conclude that these transition temperatures, though their nature is obscure, are quite as real and definite as the more usual "transformation points."

The Research Laboratories of the G. E. Co. Ltd.,  
April 1924.

XXVIII. *The Emission of  $\beta$ - and  $\delta$ -rays from a Metallic Film, and the Relation to the Quantum Theory of Scattering of X-rays.* By LEWIS SIMONS, D.Sc. (Reader in Physics in the University of London)\*.

WHEN X-rays of frequency  $\nu$  fall upon a metal plate, photo-electrons of all speeds are emitted up to a maximum speed given by  $v$  in the equation  $\frac{1}{2}mv^2 = h\nu$ , where  $m$  is the mass of the electron and  $h$  is Planck's constant. By absorbing these electrons in a layer of air at various pressures, the author succeeded in showing† that minor groups of electrons were also present possessing speeds given by the relation  $\frac{1}{2}mv^2 = h\nu - p$ , where  $p$  represents the energy associated with the K, L, M, etc. levels within the atom. The more exact photographic methods employed by de Broglie‡ and Whiddington§ have put the assumptions beyond all doubt.

When the work was resumed in London in 1922, apparatus was set up to measure by the method of a retarding electrostatic field the velocities of the slowest particles emerging. A paper on the subject|| and an earlier one by Shearer¶ are the most recent in which an attempt has been made to discover the laws of emission of the copious stream of  $\delta$ -rays, which possess an energy of comparatively few volts and which always accompany the emission of the above true photo-electrons. The general conclusions in these two papers were that the  $\delta$ -rays are many times more numerous than the rapid photo-electrons, and that they are probably produced by collision of the rapid photo-electrons with surrounding atoms. The curves clearly indicate that they form a group quite distinct from the true photo-electrons. The  $\delta$ -rays of the foregoing work had been produced by the heterogeneous beam from the tungsten anticathode of a Coolidge tube; but by working with a Wilson's tilted electroscope at great sensitiveness, the author has now succeeded in measuring the very feeble photo-electric currents

\* Communicated by the Author.

† Phil. Trans. Roy. Soc. S. Africa, viii. 1, p. 73 (1919); Phil. Mag. xli. p. 120 (1921).

‡ *Comptes Rendus*, clxxii. pp. 274, 527, 764, 806 (1921); *Journal de Physique*, p. 265 (1921). See also Report of Solvay Congress, 1921.

§ Phil. Mag. xliii. p. 1116 (1922).

|| Simons, Phil. Mag. xvi. p. 473 (1923).

¶ Phil. Mag. xlv. p. 806 (1922).

and the velocities of the  $\delta$ -electrons emerging from a thin gold film in a vacuum upon which the comparatively homogeneous fluorescent X-radiation from secondary radiators is allowed to fall.

In the meantime an interesting quantum theory of the scattering of X-rays has been worked out by Compton\*, in which he shows that if X-rays of wave-length  $\lambda_0$  fall on a scatterer, then there is an increase in wave-length due to scattering such that

$$\lambda_\theta = \lambda_0 + (2h/mc) \sin^2 \theta/2,$$

$c$  being the velocity of light and  $\theta$  the angle between the incident ray and the direction in which the same scattered ray is observed. This theory is apparently confirmed by Compton's own experiments and by others quoted in the papers, whilst still more recently de Broglie† has obtained photographic proof of the accuracy of the ideas.

Whilst plotting on the same graph—(a) the intensity of the true photo-electron emission, as above, against wave-length of the exciting X-rays, and (b) the intensity of the concomitant  $\delta$ -ray emission against the same wave-length,—it was noticed that, after suitable adjustment of ordinates, the curves could be made to coincide with each other if it could also be assumed that the X-rays responsible for the  $\delta$ -rays were in each case longer than the X-rays responsible for the true photo-electrons by 0.040 Å.U. This is precisely the value given by Compton's formula, where, in the experimental arrangements described below, the angle of scattering ranged over from  $180^\circ$  to  $90^\circ$ . It is therefore suggested that not only does the present experiment add confirmation to this theory of scattering, but that it would now appear that the true rapid photo-electrons are associated with the emission of the fluorescent X-rays or the unmodified scattered rays, whilst the  $\delta$ -rays are associated with the modified scattered rays.

#### *Apparatus and Experimental Method.*

The primary source of radiation was a Coolidge tungsten anticathode radiator pattern X-ray tube worked with a transformer. No variation whatever during working was allowed in this over the whole period of the experiments, lasting some

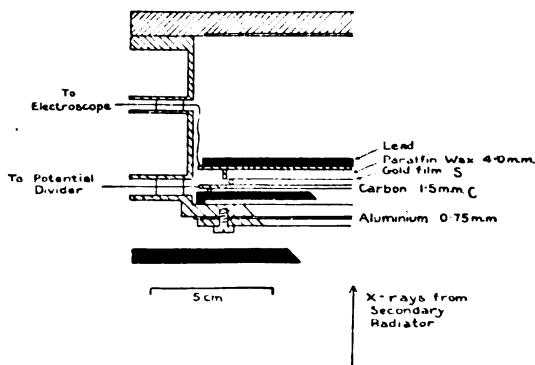
\* Phys. Rev. xxi. pp. 483-502 (May 1923); Phil. Mag. xlvi. pp. 897-911 (Nov. 1923).

† Guthrie Lecture, Physical Society of London, 1924.



months. The heating current remained constant and the tube was always worked with 3 milliamperes passing through it, equal rests being allowed between the readings. A time-factor, not a standardizing electroscope, gave the quantity of X-rays, as it was realized that these experiments deal with the fundamental processes of ionization, and therefore no method employing ionization ought to be used as a standard. The heterogeneous beam fell upon a thick secondary radiator, and the secondary fluorescent beam, limited by suitable stops, passed into the experimental chamber, half of which is shown in fig. 1. It is doubtful whether the crystal reflexion method would have any great advantage over this method, for the radiators are readily interchangeable, and if they are thick they give a fair sample

Fig. 1.



of the incident rays upon them; moreover, a large surface can be exposed to the secondary rays. The angle between the primary heterogeneous beam and the fluorescent secondary radiation was  $90^\circ$ . This secondary beam now fell normally on to an extremely thin film of gold laid down electrolytically on a plate of paraffin-wax 0.4 cm. thick, passing first through the aluminium bottom of the experimental vessel 0.75 mm. thick and a pure carbon plate 1.5 mm. thick. The lid of the vessel was sealed on with resin cerate for ease of removal, and the vessel was exhausted by a mercury-vapour pump. The mean pressure maintained during the experiments was 0.035 mm. of mercury, the pressure being measured by means of a Pirani pressure gauge. The factors deciding this pressure were the ease with which

it could be established and maintained, and the independence of the electrometer readings on small fluctuations about this mean pressure. The screen S, raised on sulphur insulators about 2 mm. from the carbon plate C, was connected by as short a wire as possible to the electrometer, which therefore registered a positive charging. A thick sheet of lead, coated with lampblack, was laid upon the top of the screen, in order to ensure that the positive charging was due only to those electrons emerging from the gold downwards.

The tilted electroscope and the method of using it as a null instrument have been described in a previous paper\*. The method ensures that the electrostatic field either retarding or accelerating the electrons remains constant and measurable, which is an obvious advantage when the fall of potential is of the order of a volt or less. The sensitiveness of the electroscope was of the order 0.007 volt per eyepiece scale division, and one-tenth of a scale division could be estimated. The capacity of the electrostatic system was about 40 cm. The time of run of the X-ray tube was varied only from 2 to 4 minutes, it being felt that larger variations than this would introduce other inaccuracies inherent in the use of a sensitive electroscope, which fails entirely, for example, in boisterous weather. As a consequence, readings were made on the same instrument without any variation which bore a ratio to each other in some cases of 20:1. The carbon plate C was finally connected to a potential divider, usually a divided megohm across which a battery was connected. The potential of C was not greater than 15 volts above or below that of S, which was maintained at earth potential.

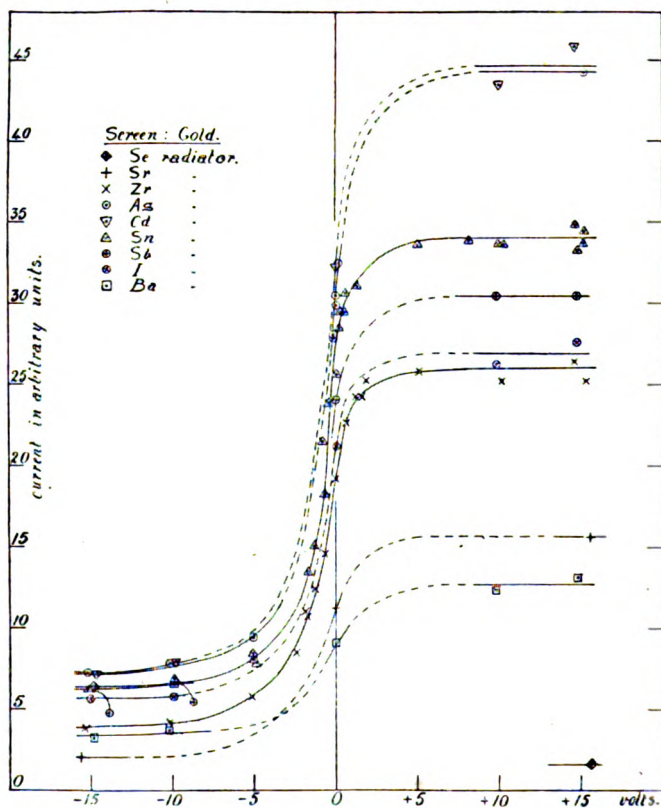
The electrons emerged from an area of S, 3 cm. in diameter, into the evacuated space between S and C, 2 mm. deep and 11.4 cm. in diameter, and the curves of the charge acquired by S in a given standard of time against the difference of potential between C and S should give a measure of the number of electrons emerging with a normal component of the energy greater than that given by this difference of potential, though undoubtedly some of the electrons are lost at the boundary. Finally, it should be stated that no measurable reading could be obtained if either the secondary radiator were removed or if the gold screen were replaced by a carbon plate.

\* Phil. Mag. xlv. p. 475 (1923).

*Experimental Results.*

Taking the greatest precautions, therefore, that conditions should be the same in all cases, fig. 2 shows the resulting curves for 9 secondary radiators used separately, the ordinates representing the positive charge acquired by S in 4 minutes, being proportional to the number of electrons emerging per second from S whose normal energy component exceeds  $eV$  when  $V$  is the potential of C.

Fig. 2.



After a careful examination of many of these curves, using different radiators and even different screens, I have concluded that the only variations they show amongst themselves are the maximum and minimum values of the electron currents, and these are intimately connected with the wavelength of the X-radiation producing them. The maximum electron emission seems to be reached at a positive potential

of C numerically smaller than the negative potential of C giving the minimum electron emission, and neither exceeds about 15 volts. Great changes in the ordinates do not occur for correspondingly large changes of potential above +15 volts or below -15 volts. All the curves seem to rise to the axis  $V=0$  very steeply and in a similar manner—in fact, by far the greater number of the electrons have a velocity of only a few volts, nor does this seem to change very much over the one and a half octaves of X-rays employed in these experiments. The conclusions drawn are (a) the difference between the maximum and minimum ordinates for each curve measures the number of the  $\delta$ - or slow rays, and (b) the minimum ordinate measures the totally distinct group of true photo-electrons or  $\beta$ -rays possessing very much greater energy. So slowly moving are many of the  $\delta$ -particles that a positive potential is required to remove many from the surface film of the metal.

Fig. 3.

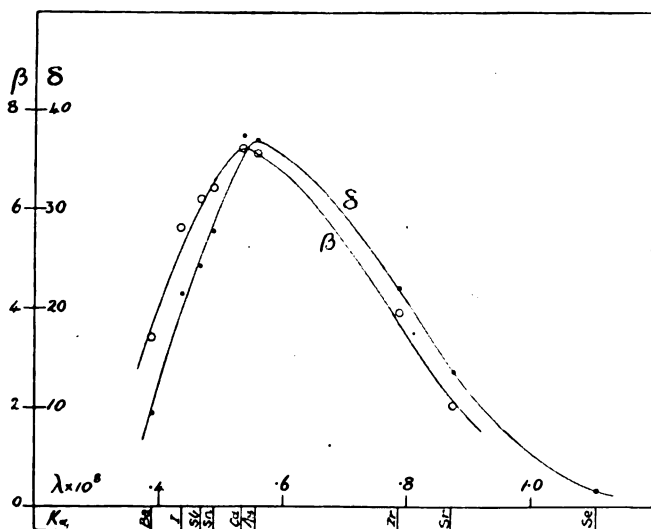


Fig. 3 shows the result of plotting (a) the differences between maximum and minimum ordinates, (b) the minimum ordinates against the wave-length of the X-rays falling on the gold film, the curve marked  $\beta$  being the minima and that marked  $\delta$  the difference between the maxima and minima. The ordinates of the  $\beta$  curve are magnified 5 times. The data are given in the table.

Dr. L. Simons on the Emission of  
Electronic Emissions from a Gold Film.

Incident X-rays from	At. No.	$\lambda_{K_{\alpha_1}} \times 10^3 \text{ cm.}$	Numbers relative and uncorrected for absorption of incident X-rays by experimental vessel.	
			$\beta$ -rays.	$\delta$ -rays.
Se .....	34	1.104	—	c. 1.7
Sr .....	38	.871	2.0	13.6
Zr .....	40	.788	3.9	22.1
Ag .....	47	.558	7.1	37.1
Cd .....	48	.534	7.2	37.4
Sn .....	50	.489	6.4	27.6
Sb .....	51	.468	6.2	24.2
I .....	53	.437	5.6	21.3
Ba .....	56	.388	3.4	9.3

The curves obviously show the characteristic shape of the intensity distribution curves for the X-radiation from a Coolidge tube obtained by the method of crystal reflexion into an ionization chamber \* before correction is made for absorption in the crystal.

The  $\beta$ - and  $\delta$ -rays therefore show the following characteristics: (a) the numbers of  $\beta$ - and of  $\delta$ -rays emitted from a thin film of gold exposed to X-rays of various wave-lengths are distributed amongst wave-lengths in a manner similar to the distribution of energy amongst wave-lengths obtained by the ionization chamber using crystal reflexion; (b) there is no constant proportionality between the number of  $\delta$ -rays and the number of  $\beta$ -rays for varying wave-lengths of incident X-rays. The ratio of  $\delta$ -rays to  $\beta$ -rays emitted per sq. cm. decreases rapidly according to a complex function as the wave-length of the incident X-rays decreases.

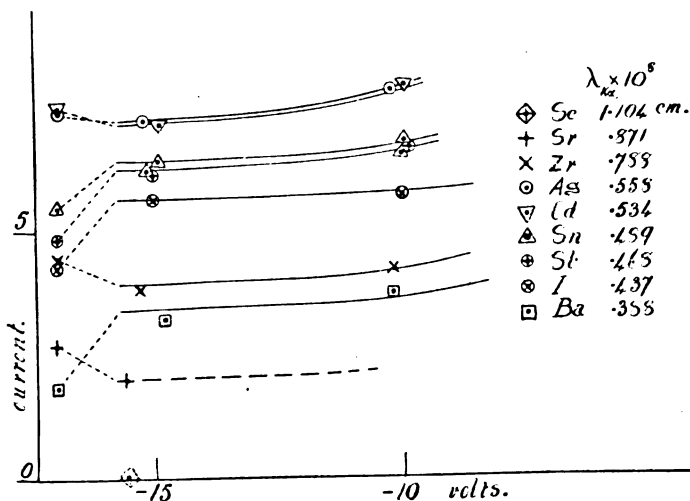
*There would, however, be strict proportionality between the  $\beta$ - and  $\delta$ -rays emerging from the gold film if each were produced by quasi-independent X-ray beams, always of the same relative intensities as measured by the number of electrons associated with each but differing in wave-length by a constant amount as the spectrum is traversed. This difference of wave-length from the graph (fig. 3) amounts to 0.040 A.U., the  $\delta$ -rays being produced by the longer wave-lengths.*

In drawing the curves for fig. 3, no attempt has been made to correct for absorption in the aluminium and carbon through which the incident rays have to pass on their way to the gold film.

\* Hull, Phys. Rev. i. p. 156 (1916); Duane & Hunt, Phys. Rev. ii. p. 166 (1915); Ledoux-Lebard et Douvillier, C. R. 1916.

Fig. 4, which represents the bottom left-hand corner of fig. 2, has been added in order to show that the relative displacement of the two curves for what I have called the  $\beta$ -rays and  $\delta$ -rays could scarcely have been brought about by a consistent error, if such existed, in the readings of the smaller currents. The points in the vertical row on the left of this figure indicate where the current-potential curves should terminate if the ratio between the numbers of  $\delta$ -rays and  $\beta$ -rays were maintained constant and equal to 5:1 as the gold film was subjected to X-rays of increasing wavelength; in other words, if the two curves of fig. 3 coincided.

Fig. 4.



The displacements are well outside the limits of experimental error in this region and, moreover, some are up and others are down. Once again, we should not expect fluctuations of this nature from the influence of the successive changes of energy of the groups of  $\beta$ -rays emerging from the gold film under the influence of the range of wave-lengths employed, as it lies well within the region  $L_{\alpha_1}$  to  $K_{\alpha_1}$  for gold.

Another point worth noting is that the emission of slow particles, thermions for example, is influenced very largely by the physical treatment of the surface of the substance emitting. No baking-out treatment has been possible. A clear indication, however, that the class of phenomenon described is a function of the metal of the screen and not of the gaseous film upon it, nor of the residual gas around it, is shown by replacing the gold film by one of another metal.

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The  $\delta$ -ray current fell to 5.8 on the same scale for a silver film, and to 2 for a tin film, using Cd  $K_{\alpha_1}$  rays. In these last results, however, a further complication is introduced by the proximity of the  $K_{\alpha_1}$  lines for silver and tin with that of the incident  $K_{\alpha_1}$  line for cadmium.

If we leave out of account the transformations that must occur at the secondary radiator and the effect of the X-radiations scattered in their passage through the aluminium and carbon bottom of the experimental vessel, and consider only the X-radiations scattered in all directions either by the gold film or by the paraffin-wax and lead behind it (though from previous work I am inclined to think that the former of these two is the more important), then the curves of fig. 3 give a measure of the total numbers of particles of the two types emerging at all angles ranging from  $180^\circ$  to  $90^\circ$  to the direction of the incident beam, and they obviously have different associations. Associating the curve for  $\beta$ -rays with Compton's unmodified scattered X-rays, and that for  $\delta$ -rays with the modified scattered X-rays, the mean change in wave-length should be given by the expression  $0.048 \times (\text{mean value of } \sin^2 \theta/2)$ , where  $\theta$  ranges over from  $180^\circ$  to  $90^\circ$   $= 0.040 \text{ \AA.U.}$ , whilst it is remarkable that the best value I can obtain from the shift between the two curves of fig. 3 is also  $0.040 \text{ \AA.U.}$  Herein may also lie the explanation of the well-known asymmetric distribution of the so-called secondary electronic radiations about a radiator.

### *Summary.*

The numbers of  $\delta$ -rays and  $\beta$ -rays emerging from the face of incidence of X-rays of varying wave-length upon an extremely thin gold film have been plotted against wave-length. The curves show that there would be strict proportionality between the  $\delta$ -rays and the  $\beta$ -rays if each were produced by quasi-independent X-ray beams rising and falling with one another in intensity, but differing in wave-length by an amount equal to  $0.040 \text{ \AA.U.}$ , the  $\delta$ -rays being associated with the longer wave-lengths. This is exactly the amount we should expect from the quantum theory of scattering of X-rays developed recently by Compton, if the  $\delta$ - and  $\beta$ -rays can be associated respectively with the modified scattered and the unmodified scattered X-rays.

My thanks are due to the Governors of Birkbeck College for a grant in aid of this research.

Birkbeck College  
(University of London), E.C. 4.

XXIX. *The Fine Structure of the Nitrogen, Oxygen, and Fluorine Lines in the Extreme Ultra-violet.* By I. S. BOWEN and R. A. MILLIKAN, *Norman Bridge Laboratory of Physics, California Institute of Technology, Pasadena* \*.

[Plate IX.]

IN the preceding studies † which carried the region of ultra-violet wave-lengths explored by vacuum grating spectroscopy down to 136 Å., our primary aim was to find what lines existed in this hitherto unexplored region, and it is altogether obvious, therefore, that we were purposely sacrificing resolution to intensity.

In order, however, to obtain the most certain interpretation of the new lines, *i. e.*, to find the optical series to which they belong, and hence the kind of ionization existing in the atoms giving rise to them, it became necessary to arrange the experimental conditions so as to be able to study with as high resolution as possible the fine structure of these lines. The reason that such a study was not at first desirable, nor, indeed, possible, is found in the fact that in order to obtain the best resolution it is necessary to go to spectra of a high order, but in order to be able to recognize a line of given wave-length in one of its high orders it is first necessary to measure, approximately at least, that wave-length by work in the first order. Such fine structure work as we are now doing, therefore, necessarily followed after such exploring work as we have already reported.

The accompanying results are obtained with "hot-spark" high-vacuum spectrometry, using a slit width of .02 mm., a 4-inch grating of 1 m. focus, with which spectra on Schumann plates in spectral orders *up to and including the tenth* have been obtained. These results represent both the highest resolution and the highest precision of wave-length determination by far which we or, so far as we know, others have as yet obtained in the region below 1000 Å.

It is estimated that the separations reported herewith may be relied upon to about .01 Å., while the absolute values of the wave-lengths may possibly be in error, on account of the uncertainty in the standards of comparison, by slightly more than this. This means that the precision of our previously published wave-lengths has been multiplied in the present work by about tenfold, and that *a set of wave-length standards correct to a few hundredths angstroms has been established in*

\* Communicated by the Authors.

† Millikan and Bowen, *Phys. Rev.* xxiii. p. 1 (1924).



the region below  $1000 \text{ \AA}$ . where no such standards have hitherto existed. In the region above  $1000 \text{ \AA}$ . the accompanying wave-lengths are somewhat less reliable because of our inability to work in higher than the third spectral order with these lines of longer wave-length.

These results could not have been obtained had not Dr. J. A. Anderson ruled for us at the Mount Wilson Observatory, in accordance with our specifications, a new 4-inch grating of very unusual quality.

Our first purpose in using as high resolution as possible was to obtain evidence as to whether the very strong oxygen line at  $844.0 \text{ \AA}$ . and also the strong nitrogen line at  $1085.2$  were not due to atoms stripped of all their valence electrons; for we had already obtained excellent evidence\* that the strongest lines in our "hot spark" were due to atoms from which the valence electrons had all been stripped off in the case of Na, Mg, Al, Si, and P, as well as in the case of Li, Be, B, and C, and we at first inferred that the very strong  $844.0$  oxygen line and the  $1085.2$  nitrogen line arose in the same way. If so, these lines all had of necessity to be doublets, since stripped atoms must all give spectra of the alkali type. Fig. 1 of the Plate presents a photograph in the fifth order, showing clearly the seven components which this line has revealed when analysed with sufficient resolution. This same structure has now been clearly shown in photographs taken in the second, third, fourth, fifth, sixth, and seventh orders. The magnification in fig. 1 is about thirtyfold.

The precision of about  $.01 \text{ \AA}$ . obtained in locating the components of this line is due to the fact that its fifth order fell close to the well-known standard barium line, the wave-length of which Fowler gives as  $\lambda = 4130.68 \text{ \AA}$ . The second order of our new boron line at  $2066.41$  and  $2067.88$  also comes exceedingly close to this standard barium line, thus enabling this strong boron line to be used as a secondary standard.

The other lines which were used as standards with which to compare some of the orders of the lines whose wave-lengths were sought were the aluminium doublets at  $1854.67$  and  $1858.13$ , and at  $1935.83$  and  $1990.50$ ; the carbon line at  $2297.59$ , and the second order of the hydrogen line at  $1215.68$ .

Plate IX. also shows a very satisfactory photograph of the structure of the strong nitrogen line at  $1085.2$ , which is here

\* Phys. Rev. xxiii. p. 33 (1924).

revealed as a quadruplet. *Neither of these two lines, 834.0 or 1085.2, is then due to stripped atoms.*

TABLE I.

<i>Oxygen.</i>			<i>Nitrogen.</i>		
Int.	$\lambda$ I. A. Vac.	$\nu$ .	Int.	$\lambda$ I. A. Vac.	$\nu$ .
1 .....	507.45	197063.7	1 .....	685.04	145976.9
1 .....	507.73	196955.1	1 .....	685.55	145868.3
1 .....	508.23	196761.3	1 .....	685.86	145802.4
1 .....	525.82	190179.1	1 .....	686.39	145689.8
1 .....	553.33	180724.0	1 .....	763.37	130998.1
1 .....	554.07	180482.6	1 .....	764.39	130823.3
1 .....	554.52	180336.1	1 .....	765.21	130683.1
1 .....	555.23	180105.5	1 .....	771.59	129602.5
2 .....	599.60	166777.9	1 .....	771.97	129538.7
1 .....	608.41	164362.8	1 .....	772.45	129454.9
1 .....	609.85	163974.7	1 .....	772.97	129371.1
1 .....	610.06	163918.3	1 .....	915.71	109204.9
1 .....	610.79	163722.4	1 .....	916.13	109154.8
1 .....	629.75	158794.8	2 .....	916.82	109072.7
1 .....	644.17	155238.5	2 .....	989.90	101020.3
2 .....	702.36	142377.1	3 .....	991.66	100841.0
3 .....	702.89	142269.8	3 .....	1084.04	92247.5
3 .....	703.90	142067.1	4 .....	1084.60	92199.9
3 .....	718.56	139167.2	3 .....	1085.59	92115.8
1 .....	779.86	128228.1	4 .....	1085.75	92102.2
2 .....	787.74	126945.4	1 .....	1134.20	88167.9
2 .....	790.22	126547.0	1 .....	1134.45	88148.4
1 .....	796.69	125519.3	1 .....	1135.02	88104.2
3 .....	832.78	120079.7	2 .....	1492.83	66986.9
3 .....	832.95	120055.2	2 .....	1494.78	66899.5
4 .....	833.35	119997.6	<i>Fluorine.</i>		
4 .....	833.77	119937.2	605.64	165114.6	
4 .....	834.48	119835.1	606.23	164955.5	
2 .....	835.12	119743.3	606.83	164790.8	
4 .....	835.31	119717.2	607.43	164628.0	
			607.99	164476.4	
			656.00	152439.0	
			656.34	152360.1	
			656.84	152244.1	
			657.69	152047.3	
			658.31	151904.1	

Table I. shows the structure and wave-length of all save the very weakest of the oxygen, nitrogen, and fluorine lines  
*Phil. Mag.* S. 6. Vol. 48. No. 284. Aug. 1924. T

which appear upon our plates. It will be seen that the frequency separation of the lines of the 507 triplet is quite the same as that of the 703 triplet, thus indicating an identity of origin—an origin which will be shown in a later paper to be  $O_{III}$ .

The structure of the two fluorine lines is not as certain as are the other structures shown.

Table I. contains the fine structure of all of the strong lines of wave-length below 1500 Å. which are due to any of the atoms up to neon, except those due to carbon and to boron. The fine structures of all the boron lines have been analysed in a preceding paper \* and definitely assigned to  $B_{III}$ ,  $B_{II}$ , and  $B_I$ .

As to the strong lines of carbon, previous to this analysis with high resolution we had been inclined to regard the very powerful carbon line at 1335 Å. as arising from the stripped atom of carbon, for it had been found to be a doublet, and it also had other characteristics which we had associated with stripped atoms†. Doubt had been thrown upon this conclusion, however, by the fact that Simeon‡ had obtained this line in both a 30-volt arc and a 40-volt arc, and such an arc should not give rise to a stripped atom of carbon. A further comparison of the intensities of the 1335 doublet with the 1550 carbon doublet brought out quite convincing evidence that it was the latter instead of the former which had its origin in the stripped atom of carbon.

This argument, from the point of view of intensity, is contained in the following table:—

TABLE II.

Line.	Old.	New.	Simeon.			Hutchinson.	
			220 v.	40 v.	30 v.	H.-spk.	110 v. arc.
1335 .....	15	2, 6, 5, 5, 4, 2	10	Obs.	Obs.	8	10
1550 .....	5	4, 5, 6, 5, 5, 3	3	...	...	3	...

The column labelled "old" represents results obtained with electrodes of carbon which could be separated as much as 2 or 3 mm. and which gave sparks having a rather "arc-like" character, while the columns headed "new" correspond to observations made with aluminium electrodes in which carbon was merely an impurity. The spark here passed with difficulty and was a true "hot spark." It is to

\* Proc. Nat. Acad. Sci. May 15, 1924.

† Phys. Rev. xxiii. p. 33 (1924).

‡ Proc. Roy. Soc. civ. p. 373 (1923).

be noted that in all these new observations the 1550 line has gained largely in intensity relative to the 1335 line, being actually the stronger line in most of them. *Line 1550 Å. thus clearly corresponds to a higher state of ionization than does line 1335 Å.* Also Simeon's\* and Hutchinson's† data are consistent in revealing the 1335 line in arcs, while it is only in the "high potential arc" or the hot spark that the 1550 line appears at all.

The foregoing evidence is beautifully supported by the progression of the doublet separation of the  $p_1 p_2$  terms shown by the stripped-atom spectra in the group of elements from lithium to carbon shown in Table III. The 1335 line does

TABLE III.

	$\lambda(2s-2p).$	$\nu.$	Differences.	$\Delta\nu.$	$\frac{\Delta\nu}{(N-2)^4}.$
Li .....	6707·85	14903·8		·338	·338
			17023·8		
Be .....	3131·194	31927·60		6·61	·413
	3130·546	31934·21	16431·1		
B .....	2067·88	48358·7		34·4	·425
	2066·41	48393·1	16122·6		
C .....	1550·84	64481·2		107·4	·420
	1548·26	64588·6			

not fit into this progression at all, as does the 1550 line, for its doublet separation  $\Delta\nu$  is 67 instead of 107, which makes the corresponding number of the last column come out ·262 instead of ·420, the latter of which alone is consistent with the other numbers given in this last column. Also the equality of "differences" shown in the fourth column is entirely destroyed if line 1335 is inserted in place of line 1550.

*The doublet separation shown in the last two columns of the table not only increases as the fourth power of the effective nuclear charge, but its numerical value is closely predicted by the relativity, or regular, doublet law, which is already known to give the separation of the regular X-ray doublets.*

The linear progression of frequencies shown in the fourth column is a result of the fact that the separation of the  $s$  and  $p$  terms in all these spectra follows the law of the irregular X-ray doublet. Indeed, we have found by a study with high resolution like that shown in the plate, of the fine structure of the doublets and triplets in our extreme ultra-violet spectra, *that the X-ray doublet laws are applicable to the whole field of optics as well as to that of X-rays.*

\* Simeon, Proc. Roy. Soc. civ. p. 373 (1923).

† Hutchinson, Astro. Phys. Jr. lviii. p. 291 (1923).

We have also obtained unimpeachable proof that our "hot spark" produces the whole series of stripped atoms  $\text{Li}_I$ ,  $\text{Be}_{II}$ ,  $\text{B}_{III}$ ,  $\text{C}_{IV}$ ,  $\text{N}_V$ ; also  $\text{Na}_I$ ,  $\text{Mg}_{II}$ ,  $\text{Al}_{III}$ ,  $\text{Si}_{IV}$ ,  $\text{P}_V$ ,  $\text{S}_{VI}$ , as well as other series of similar atomic structure like  $\text{B}_I$ ,  $\text{C}_{II}$ ,  $\text{N}_{III}$ ,  $\text{O}_{IV}$ . *Indeed, we have definitely identified lines due to all of the foregoing atoms.* The analysis leading to these conclusions is to appear in detail in a forthcoming paper in the 'Physical Review,' entitled "The Extension of the X-Ray Doublet Laws into the Field of Optics." The main purpose of the present paper is to show the sort of resolution and the accuracy of wave-length determination which we are attaining in the new studies which we are now making of all the stronger lines, the wave-lengths of which we had located approximately in our preceding studies of extreme ultra-violet spectra.

XXX. *Surface Tension of Colloidal Solutions and Dimensions of certain Organic Molecules.* By P. LECOMTE DU NOÛY, *Sc.D.\**

[From the Laboratories of the Rockefeller Institute for Medical Research.]

A LARGE number of papers have been published on the surface tension of colloidal solutions; but, owing to the methods used, certain facts have been overlooked so far. The purpose of this paper is to review briefly the results obtained by using a different method, namely, the pull on a ring. By this method, the surface tension of the same layer of liquids may be measured, at intervals of time, instead of that of a continuously renewed layer †.

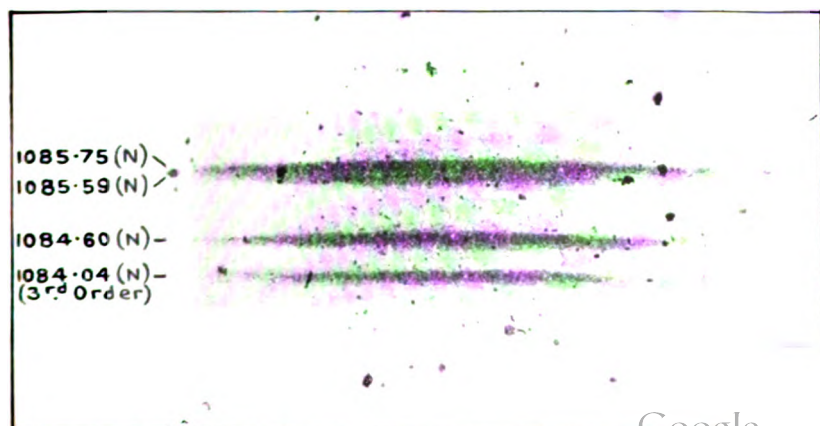
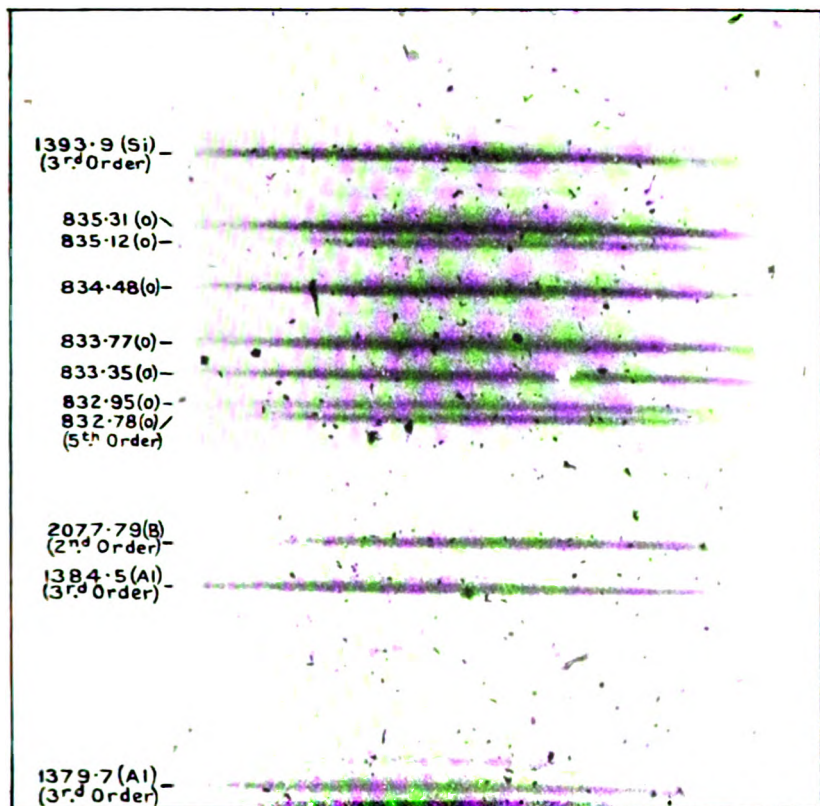
EXPERIMENTAL.

It will suffice to say that the instrument used, based on the work of Weinberg ‡, has been described by the writer

\* Communicated by the Author.

† du Noüy, P. L., J. Exp. Med. xxxv. pp. 575, 707; xxxvi. pp. 115, 547 (1922); xxxvii. p. 659; xxxviii. p. 87 (1923); xxxix. p. 37 (1924). ("Surface Tension of Serum, VIII. Further Evidence on the Existence of a Superficial Polarized Layer of Molecules at Certain Dilutions.") J. Exp. Med. 1924, in press.—("Surface Tension of Serum, X. On the Thickness of the Monomolecular Layer of Serum.") J. Exp. Med. 1924, in press.—("On the Surface Tension of Colloidal Solutions and the Size of Some Colloidal Molecules.") Read before the American Physical Society, Feb. 23, 1924, in press.

‡ Weinberg, B., *Zeit. f. Phys. Chem.* x. p. 34 (1902).





in the 'Journal of General Physiology'\*, by Sir William Bayliss†, and by Holmes‡. The torsion of a wire controlled by a worm-gear is used to counteract the stress of the liquid film adhering to a platinum ring, and as the amount of torsion can be measured by a simple reading on a dial, the surface tension is measured directly. The measurements require only 20 seconds. Those reported in this paper were made at a temperature of  $23 \pm 0.5^\circ \text{C}$ . Two cubic centimetres of liquid in watch-glasses were used, the diameter of the free surface being very nearly 4 cm. The glassware, containers, flasks, pipettes, watch-glasses, etc., were freshly boiled for two hours in a cleaning solution (sulphuric acid and potassium dichromate), rinsed in specially prepared distilled water, and dried. No alcohol or ether was ever used. When NaCl was used for preparing the solutions of serum, for example, it was washed, then recrystallized twice. The greatest care was taken in handling the solutions under experiment, so as not to disturb their surface. A special table was built on which the surface tension apparatus, supported on a small carriage, was rolled on rigid rails, in front of every solution in succession. Under such conditions about 38,000 measurements were made, and the following results, which will be summarized rapidly, were obtained.

I. The surface tension of colloidal solutions is not constant but decreases rapidly as a function of the time. So far, no colloidal solutions have been found which do not show this phenomenon. Experiments have been carried out mainly with blood serum, pure albumen, hemoglobin, globulins, sodium oleate, sodium glycocholate and taurocholate, and saponin solutions, a great number of dyes, and gold, silver, copper, and iron sols (electrically prepared). The drop varies, of course, according to the substances and to the concentration. It is much smaller in the electrosols mentioned above. At a given concentration, it can be expressed by the formula (figs. 1 and 2)

$$\gamma = \gamma_0 e^{-Kt^{\frac{1}{3}}}$$

until a certain stable value is attained. This phenomenon is due to the adsorption in the surface layer, in function of time, of the molecules in suspension. As the concentration of the solution in every watch-glass does not vary, this phenomenon seems to differ from ordinary adsorption which

\* du Noüy, P. L., *J. Gen. Physiol.* i. p. 521 (1919)

† Sir William Bayliss, 'The Colloidal State,' London, 1923, p. 65.

‡ Holmes, H. N., 'Laboratory Manual of Colloidal Chemistry,' New York, 1922, p. 52.



is regarded as almost instantaneous. However, it may be assumed that in these colloidal solutions the concentration varies proportionally to the time as the adsorption progresses.

Fig. 1.

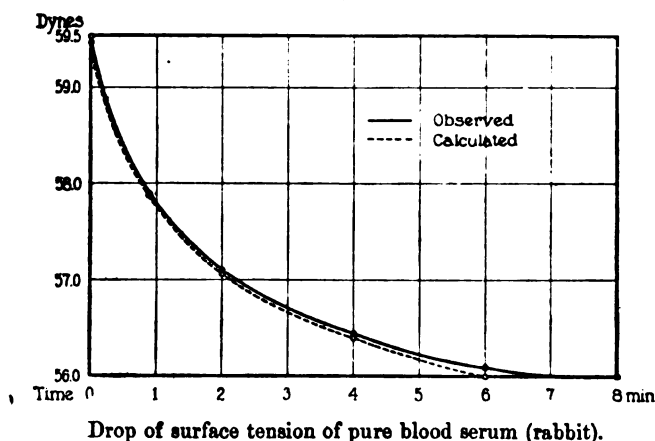
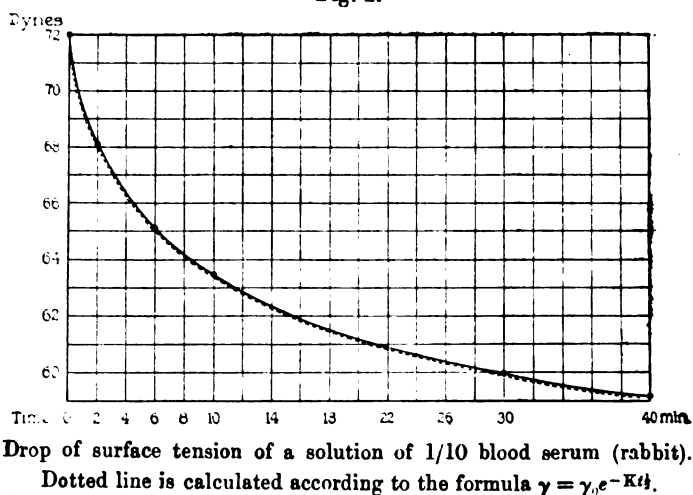


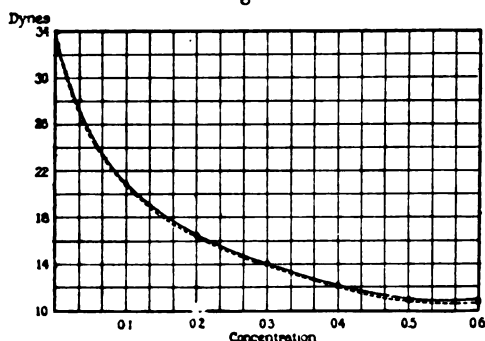
Fig. 2.



This assumption is supported by the fact that the same formula, in which  $t$  is replaced by  $c$  (concentration), satisfactorily fits such adsorption isotherms as published by

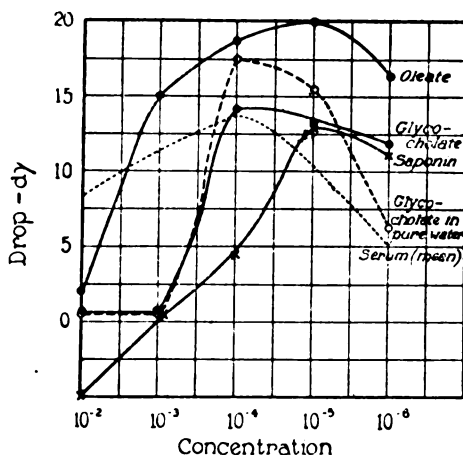
Lewis\*, expressing the adsorption of sodium glycocholate by paraffin oil (Table I. and figs. 1 and 3). Fig. 4 gives an

Fig. 3.



Action on surface tension of adsorption of sodium glycocholate by paraffin oil (Lewis).

Fig. 4.



Time-drop of the surface tension of certain colloidal solutions, in function of their concentration.

\* Lewis, W. C. McC., Proc. Physic. Soc. xxi. p. 150 (1909); Phil. Mag. xvii. p. 466 (1909); Zeit. Chem. u. Indust. Kolloide, v. p. 91 (1909); also cited by Willows, R. S., and Hatschek, E., 'Surface Tension and Surface Energy, and their Influence on Chemical Phenomena.' Philadelphia, 1915, p. 41.

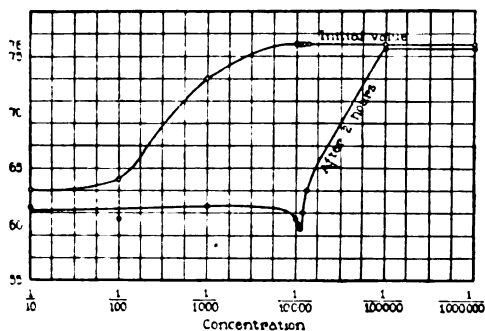
idea of the phenomenon as a function of the concentration for a few substances. It is to be noticed that a sodium oleate solution in such quantities as  $10^{-5}$ , although it affects the initial surface tension of water very little, will cause a drop of more than 25 dynes in two hours. The drop in the surface tension of sodium oleate at higher concentrations has been observed before, but could not be followed step by step on account of the methods used, and was not thought to be a general phenomenon of colloids. The effect of dilution was also overlooked. One-millionth part of sodium oleate does not affect the initial surface tension of water, but causes a drop of 20 dynes in two hours. The drop weight or drop count methods are unable to show this phenomenon.

II. In all the cases studied (organic colloids), a decided minimum value was observed at a given concentration. Under the conditions of our experiments, it occurred around 1/750,000 for sodium oleate, 1/117,200 for crystalline egg albumen, and 1/10,500 for rabbit serum, and as this serum contained 6.51 per cent. of proteins, the final dilution was near 1/160,000. On both sides of this minimum (fig. 5) the drop is smaller. In the case of certain strongly active substances (saponin, etc.), it often happens that, at low dilutions (1/10 to 1/1000), a slight increase is observed instead of a drop. An hypothesis was made in order to account for the maximum drop. At this optimum concentration (the size and shape of the vessels in which the solutions were exposed being taken into consideration), the existence of a monomolecular and oriented layer was assumed; such a layer is only possible at one concentration for every orientation of the molecule in the same vessels, and its geometric organization would account for the existence of the smallest possible field of forces compatible with the number of free molecules in the solution. Figs. 5 and 6 show how well defined and sharp this minimum is in the case of serum and sodium oleate. A more careful investigation on both sides of this minimum revealed the presence of two more minima. One of these probably corresponds to a monolayer (the writer proposes this term instead of "monomolecular layer") of horizontal molecules. Experiments are being carried out on this subject at present.

III. If the solutions are stirred, even slightly, after standing, the surface tension rises and reaches a value generally smaller than the initial value (fig. 7). This phenomenon can be repeated a number of times, and for this

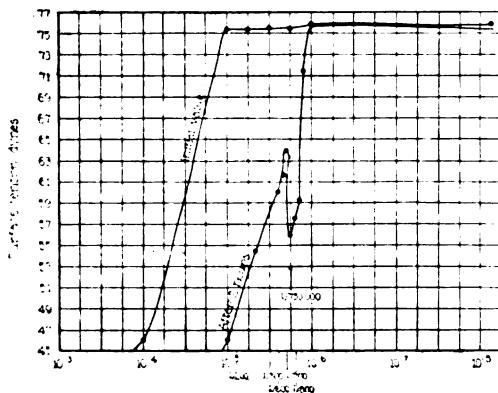
very reason great care must be taken when the time-drop is being measured. In the case of the biological colloids (blood

Fig. 5.



Initial values and values after two hours of the surface tension of solutions of serum.

Fig. 6.

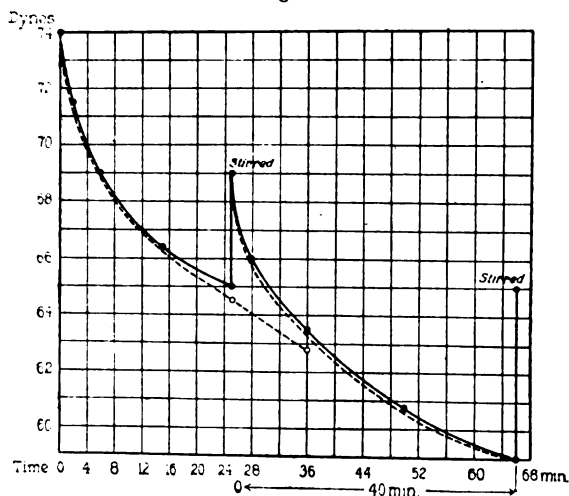


Initial values and values after two hours of the surface tension of sodium oleate solutions in water. Between  $10^{-3}$  and  $10^{-6}$ , the figures representing concentrations should be divided by 1000, namely,  $\frac{1}{200,000}$ ,  $\frac{1}{500,000}$ , etc. Space did not allow more figures on the chart.

serum) studied, after some time (48 hours), the solution became practically inert when it had been stirred frequently and there was no further rise after stirring.

IV. Should the above assumption of the existence of a homogeneous oriented monolayer at a given concentration be well founded, the rate of evaporation of such a solution should be slower than that of any other concentration.

Fig. 7.



Rise in surface tension when solution is stirred.

Water molecules would not escape so freely from a solution covered with such a film. At a higher concentration, we have assumed that there is a piling up, and no organization of the molecules. Therefore, the water molecules can pass between and escape more easily than through a closely-fitting mesh of identically oriented molecules. At lower dilutions, the breaks in the film would allow the normal process of evaporation to take place. Experiments proved that, with the colloidal solution tested (blood serum), such was the case. The results of a series of experiments are given in Tables II. and III.

So far, our assumption seems to be supported by the facts. It is very plain in these tables that solutions at  $1/10,000$  evaporated more slowly than the others. An interesting conclusion may be drawn from these experiments on serum. Of course, the critical concentration  $10^{-4}$  is a function, among other things, of the ratio  $\frac{\text{surface}}{\text{volume}}$  of the vessels in which the solutions are exposed. In the case of our watch-glasses, this ratio is 12, if it is assumed that adsorption takes

TABLE I.

Agreement between Figures Observed and Calculated for the Lowering of Surface Tension at the Interface between a Solution of Sodium Glycocholate and Paraffin Oil, in Function of the Concentration (fig. 3).

$$K = 0.222.$$

Concentration, per cent.	0	0.1	0.2	0.3	0.4	0.5	0.6
Surface tension observed (Lewis), dynes .....	34.0	21.0	16.5	14.0	12.2	11.0	10.9
Surface tension calculated $\gamma = \gamma_0 e^{-Kc}$ , dynes .....	—	20.2	16.5	14.0	12.2	10.9	9.7

TABLE II. (ser. No. 1).

Diameter of Serum Solutions (Rabbit) evaporating in Watch-Glasses.

Dilution.	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$
Diameter in mm. at 5.41 P.M., after 6 hours' evaporation ...	26	27	27	30	27	26
30 minutes later .....	20	20	23	26.5	23	22
1 hour later .....	0	0	6	14	0	0

TABLE III. (ser. No. 2).

Diameter of Serum Solutions (Rabbit) evaporating in Watch-Glasses.

Dilution.	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$
Diameter in mm. at 5.42 P.M. ....	18	23	21	21	20	20
50 minutes later .....	0	5	8	12	0	0

place on the glass, as will be shown later. Should the surface increase with respect to the volume (as happens when the volume decreases), this ratio would become very great. If we attempt to calculate the size of the vessels which would require pure serum to develop such a monolayer,

in other words, in which the ratio  $\frac{S}{V}$  would be equal to 134,000 instead of 12 (the serum being diluted to 1/11,000), it is found that they would have to be of the order of magnitude of the blood capillaries, filled with blood cells. Thus, one of the factors governing the concentration of colloids in the serum is found. The adsorption of molecules

of substances such as albumens and proteins in general (biological colloids) and sodium oleate takes place on the glass in a similar way as on the free liquid surface. This was ascertained in the following manner :—

Two series of watch-glasses were prepared ; in one series, 500 very small glass beads were placed side by side. The surface of the glass was thus increased by 14.2 sq. cm. The same set of solutions (rabbit serum at the following concentrations : 1/5000, 1/6000, 1/7000, 1/8000, 1/9000, 1/9500, 1/10,000, 1/10,500, 1/11,000, 1/11,500, 1/12,000, and 1/13,000) was placed in the two sets of watch-glasses.

Without beads, the ratio  $\frac{S}{V}$  equalled 12.8. With the beads,

the volume of the liquid being the same, this ratio became 19.9. If our assumption is correct and provided adsorption takes place on the glass, the maximum drop must be shifted towards a higher concentration, and its place will be at a

concentration  $\frac{19.9}{12.8} = 1.56$  greater, namely, at 1/7000 instead

of 1/11,000. The experiments supported this view entirely, and the maximum drop, as well as the minimum value of the surface tension, occurred at 1/7000 in the watch-glasses with beads.

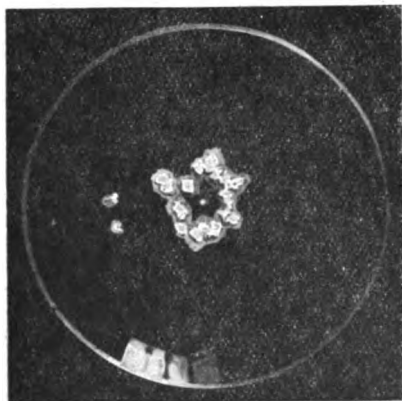
The existence of such a criterion (namely the minimum of surface tension) for a monolayer makes it possible to compute its thickness, if the concentration at which it occurs is accurately known. Fig. 5 shows that this value is very well defined. The specific gravity of anhydrous proteins of the serum was measured and found equal to 1.275. On such a basis, the thickness of a monolayer of serum proteins was found to be  $38.5 \times 10^{-8}$  cm. The length of the molecule of crystalline egg albumen was found to be  $52.8 \times 10^{-8}$ , and if its molecular weight is assumed to be 34,000 (Sørensen), and Millikan's value for  $N$ ,  $6.06 \times 10^{23}$ , is taken, we find the square root of the cross-section of this molecule to be  $29.2 \times 10^{-8}$ . Hence, it would seem to be oriented vertically. The same technique and calculation applied to a substance whose molecular weight is well known, such as sodium oleate, yielded the following figures (the minimum value of the surface tension occurs at 1/750,000, and the molecular weight is 304). The calculated length of the molecule is found to be  $12.3 \times 10^{-8}$  cm., and the square root of the cross-section  $6.8 \times 10^{-8}$  cm.

If we compare these figures with the dimensions of the

molecule of oleic acid, as given by Langmuir (length,  $11.2 \times 10^{-8}$ ; square root of cross-section,  $6.8 \times 10^{-8}$ ), we see that the diameter of the molecule is unchanged, but that its length is increased by  $1.1 \times 10^{-8}$  cm. This would correspond to the space occupied by the sodium atom at the end of the molecule. When the length of insoluble organic molecules (oleic acid, tripalmitine, tristearin, cetyl palmitate, myricyl alcohol, etc.) is divided by the number of carbon atoms, the length per carbon atom is obtained. The mean value of this length, for nine substances, is equal to  $1.4 \times 10^{-8}$  cm. As the sodium oleate molecule is dissociated, a double electric layer is probably formed at the surface, the free  $\text{Na}^+$  ions being energetically attracted by the powerfully negative film due to the identical orientation of the oleic<sup>-</sup> ions in the surface layer.

V. When a solution of NaCl (0.9 per cent.) is allowed to crystallize in a perfectly clean watch-glass, the crystals are formed at the bottom and grow as evaporation takes place. They finally assume the appearance shown in fig. 8. When

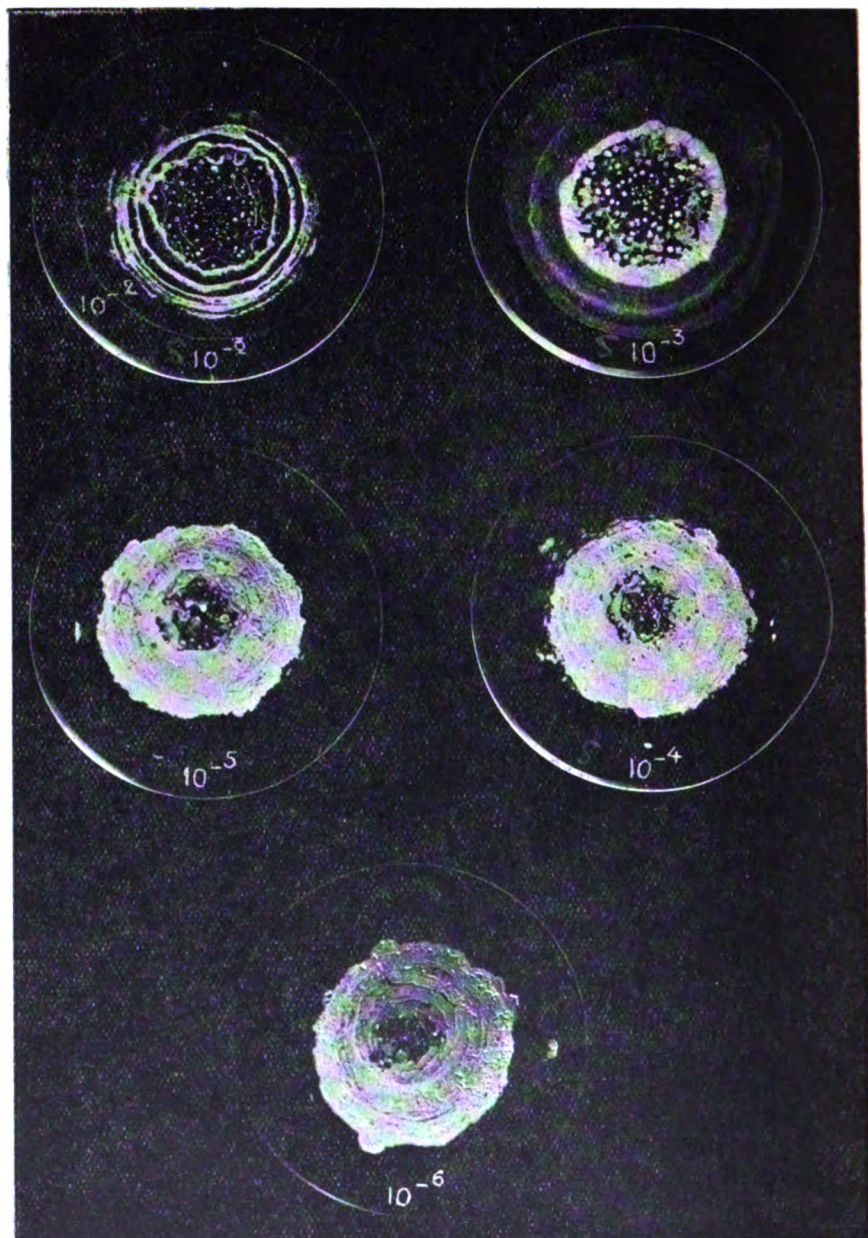
Fig. 8.



Crystals of pure sodium chloride : 2 c.c. of a 0.9 per cent. solution in a watch-glass.

a small amount of any colloid is added to such a solution, concentration in the bulk no longer takes place, large crystals are not formed, and the sodium chloride (or any other salt of the same kind) is deposited on the walls of the watch-glass in a thin, smooth, and often opaque, white layer of very small crystals (fig. 9). At the bottom, a darker area with a few tiny scattered crystals indicates that concentration did



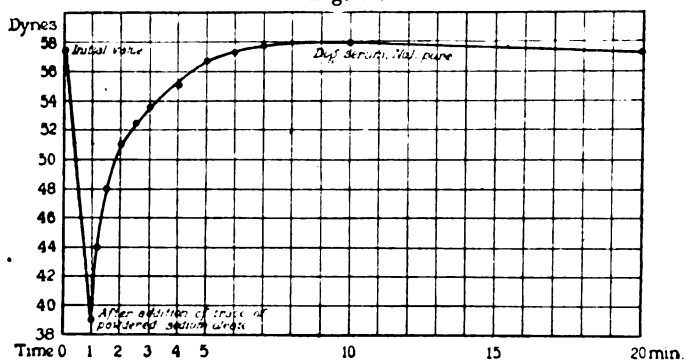


Sodium chloride crystals in watch-glasses. A small amount of saponin has been added to a 0.9 per cent. NaCl solution. The concentration of saponin is  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ , and  $10^{-6}$ .

not take place, and that the molecules and ions are first being adsorbed on the colloidal micellæ, then carried up to the surface layer. As evaporation progresses, the colloidal particles, with their adsorbed NaCl, are deposited on the glass in concentric beaches. At certain concentrations, periodic rings are to be observed; at 1/100, for example, in the case of serum, and 1/1000 for saponin and sodium oleate. The appearance of the crystals is quite characteristic of the concentration, and varies but little. Thus, in the case of a composite solution of colloids and crystalloids, Gibbs' law, which states that substances tending to increase surface tension will concentrate in the bulk, no longer holds true. This observation has thrown light on the spontaneous creation of membranes at interfaces which was difficult to explain before the discovery that not only colloids but also crystalloids concentrated in interfaces at the same time.

VI. When two colloids are present in the same solution, one of the factors governing the final surface tension of the

Fig. 10.



Recovery of the surface tension of a colloidal solution (dog serum pure) to which a trace of powdered sodium oleate was added.

solution is the adsorption equilibrium existing between the two. The following experiment will make this clear. If a trace of powdered sodium oleate (about 1/10,000 in weight) is added to a less surface-active colloid in solution, such as proteins, gelatin, gum arabic, or metallic sols, the surface tension drops instantaneously by about 50 per cent., then immediately starts rising again until a certain equilibrium (which may be called adsorption equilibrium) is attained. In certain cases (pure blood serum, for example), the final surface tension is equal to the original value before the addition of sodium oleate. In order to observe this phenomenon, measurements must be made every 30 seconds, or at least every minute (fig. 10).

The curve representing the phenomenon is again a logarithmic one. Let us call A the relatively inert colloid to which the surface active colloid B is added. When B is added in solution instead of powdered, or when the solution is stirred after its addition, the surface tension does not rise so high, as a greater number of micellæ of colloid A are coated with colloid B. When powdered sodium oleate (A) is added without stirring, a relatively small number of micellæ of colloid B are heavily coated with A, and in time practically all of A is adsorbed on a few B micellæ which either precipitate or collect in large aggregates with little action on surface tension. This buffing or antagonistic action of colloids seems to be a general phenomenon.

#### SUMMARY.

The use of an instrument allowing measurements of the surface tension of the same layer of liquids at very short intervals (15 to 30 seconds) made it possible to study the evolution of certain surface tension phenomena in function of time, namely :

1. The spontaneous drop of the surface tension of all colloidal solutions, with the order of magnitude of 1 dyne per minute during the first minute. This drop increases with dilution and shows a maximum at a given concentration, varying between  $10^{-4}$  and  $10^{-5}$  generally. The drop may then reach 20 dynes for colloids such as blood serum and albumen, which were not considered as acting powerfully on the surface tension of water. Certain colloids, saponin, for instance, do not show any drop at high concentrations, but even a slight increase ( $10^{-1}$  to  $10^{-3}$ ).

2. When such solutions are stirred, the surface tension rises.

3. The existence of an accurate criterion of the existence of a monolayer at a well-known concentration makes the calculation of the thickness of such a layer possible. This criterion—minimum value—does not always coincide with the maximum drop. In the case of pure soluble substances (albumens, etc.), it gives the length of the molecule, and, when the molecular weight is known, its cross-section can be calculated. The length of the molecule of sodium oleate was found to be  $12.3 \times 10^{-8}$  cm. and its width  $6.8 \times 10^{-8}$  cm. The length of serum albumen was 43.3, and that of egg albumen  $52.8 \times 10^{-8}$  cm.

4. The crystallization of sodium chloride solution, or

other salts, is affected by even the presence of one-millionth part of most colloids, and large crystals do not form at the bottom of a watch-glass. On the contrary, as the ions are adsorbed on the surface, the NaCl molecules are deposited in fine crystals along the walls of the glass, and form periodic rings at certain concentrations.

5. Evaporation of serum solutions in watch-glasses is slower at a dilution of  $10^{-4}$  than at any other concentration. This fact is explained by the assumption made in order to account for some phenomena reported above (1), namely, the existence of a monomolecular oriented layer at a given concentration.

6. When sodium oleate or any surface active colloid is added to another more inert colloidal solution, such as pure serum, for instance, the surface tension drops considerably, then rises immediately, and may reach its initial value in 7 minutes.

XXXI. *Central Orbits in Relativistic Dynamics treated by the Hamilton-Jacobi Method.* By G. TEMPLE, B.Sc., Birkbeck College \*.

#### *Introduction.*

THE first part of this paper is devoted to an exposition of a process of integration applicable in particle dynamics on any relativistic theory, and forming the appropriate generalization of the methods of Hamilton and Jacobi in classical mechanics. In the second part, this method is applied to the problems of planetary motion and of the deviation of rays of light in the solar field according to the theories of Einstein and Whitehead.

In the treatment of the Bohr hydrogen atom according to the restricted theory of relativity, Sommerfeld (14) and (15) has made use of this method, but so far it has not been employed in the general theory of relativity.

#### *Canonical Equations for Particle Dynamics.*

1. Let  $(x_1, x_2, x_3, x_4)$  be a "pure" system of coordinates, and let

$$ds^2 = \sum_{\mu, \nu} g_{\mu\nu}^{(x)} \cdot dx_\mu \cdot dx_\nu$$

be the fundamental differential form of the metric manifold.

\* Communicated by Prof. A. N. Whitehead, F.R.S.

*Phil. Mag.* S. 6. Vol. 48. No. 284. Aug. 1924.

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Then the equations to an historical route can be written in the form

$$x_\mu = x_\mu(\lambda), \quad \mu = 1, 2, 3, 4,$$

where the four functions  $x_\mu(\lambda)$  are single-valued, differentiable, and satisfy the inequality

$$\sum_{\mu, \nu} g_{\mu\nu}^{(x)} \cdot dx_\mu(\lambda) \cdot dx_\nu(\lambda) \geq 0.$$

Let

$$x'_\mu = \frac{dx_\mu(\lambda)}{d\lambda}, \quad \mu = 1, 2, 3, 4,$$

and let

$$E = \sum_{\mu, \nu} J_{\mu\nu}^{(x)} \cdot x'_\mu \cdot x'_\nu,$$

where  $\|J_{\nu\mu}^{(x)}\|$  is a symmetrical covariant tensor of the second order, and

$$dJ^2 = \sum_{\mu, \nu} J_{\mu\nu}^{(x)} \cdot dx_\mu \cdot dx_\nu$$

is the fundamental differential invariant of the dynamic manifold.

The integral

$$I = \int_{\lambda=\lambda_1}^{\lambda=\lambda_2} E \cdot d\lambda$$

taken along an historical route joining the event-particles whose parameters are  $\lambda_1, \lambda_2$  together with its first variation,

$$\delta I = \sum_{\lambda=\lambda_1}^{\lambda=\lambda_2} \left( \frac{\partial E}{\partial x_a} - \frac{d}{d\lambda} \frac{\partial E}{\partial x'_a} \right) \delta x_a \cdot d\lambda + \sum_a \left[ \frac{\partial E}{\partial x'_a} \right]_{\lambda=\lambda_1}^{\lambda=\lambda_2},$$

is defined even when  $dJ=0$  and  $E=0$ .

If  $dJ \neq 0$ , we may identify the parameter  $\lambda$  with the integral

$$\int^\lambda dJ$$

taken along the historical route from some arbitrary fixed event-particle to the event-particle whose parameter is  $\lambda$ .

Then

$$\delta I = -2 \int_{\lambda=\lambda_1}^{\lambda=\lambda_2} \sum_{\alpha} \left[ \sum_{\mu} J_{\mu\alpha}^{(x)} \cdot \ddot{x}_{\mu} + \sum_{\mu,\nu} J_{\alpha}^{(\mu\nu)} \cdot \dot{x}_{\mu} \cdot \dot{x}_{\nu} \right] \delta x_{\alpha} \cdot d\lambda \\ + \sum_{\alpha} \left[ \frac{\partial E}{\partial \dot{x}_{\alpha}} \right]_{\lambda=\lambda_1}^{\lambda=\lambda_2},$$

where  $\dot{x}_{\mu} = \frac{dx_{\mu}}{dJ}, \quad \ddot{x} = \frac{d^2 x_{\mu}}{dJ^2}.$

Since  $E = \left( \frac{dJ}{d\lambda} \right)^2$  the first variation of the integral will vanish if the functions  $x_{\mu}(\lambda)$  are chosen to satisfy the equation

$$\sum_{\mu,\nu} J_{\mu\nu}^{(x)} \cdot x'_{\mu} \cdot x'_{\nu} = 0.$$

It has been shown in a paper by Murnaghan (1) that the functions satisfying this equation are the limiting forms assumed by the functions satisfying the more general equation

$$\delta I = 0,$$

as  $dJ$  (and  $E$ ) tends towards zero.

This investigation is necessitated by the indeterminate character of the operator  $\frac{d}{dJ}$  when  $dJ=0$ .

2. Let  $\|A_{(x)}^{\sigma}\|$  denote the components of the contravariant acceleration tensor

$$\left\| \ddot{x}_{\sigma} + \sum_{\alpha,\beta} J \left\{ \begin{matrix} \alpha\beta \\ \sigma \end{matrix} \right\} \dot{x}_{\alpha} \dot{x}_{\beta} \right\|, \quad \sigma = 1, 2, 3, 4,$$

and let  $\|F_{\mu}^{(x)}\|$  denote the components of the electromagnetic vector potential, which satisfy the equation

$$\sum_{\mu} \frac{\partial F_{\mu}^{(x)}}{\partial x_{\mu}} = \sum_{\mu,\rho} F_{\rho}^{(x)} \cdot J \left\{ \begin{matrix} \mu\mu \\ \rho \end{matrix} \right\} \dots$$

Let

$$F_{\alpha\beta}^{(x)} = \frac{\partial F_{\alpha}^{(x)}}{\partial x_{\beta}} - \frac{\partial F_{\beta}^{(x)}}{\partial x_{\alpha}}, \quad \alpha, \beta = 1, 2, 3, 4$$

and

$$F_{\alpha}^{\sigma(x)} = \sum_{\beta} J_{(x)}^{\beta\sigma} \cdot F_{\alpha\beta}^{(x)}, \quad \alpha, \sigma = 1, 2, 3, 4.$$

$\|J_{(x)}^{\mu\nu}\|$  being the contravariant associate of  $\|J_{\mu\nu}^{(x)}\|$ .

Then the equations of motion of a particle of proper mass  $m$  and charge  $e$  may be written in the form

$$m \cdot A_{(x)}^{\sigma} + \frac{e}{c} \sum_a F_a^{\sigma(x)} \dot{x}_a = 0, \quad \sigma = 1, 2, 3, 4$$

in all theories of Relativity ( $c$  being a constant).

3. These equations are equivalent to equations (11) on p. 80 of 'The Principle of Relativity,' by A. N. Whitehead, and may be deduced, as in the book, as a condition of the vanishing of the first variation of the integral

$$\int_{\lambda=\lambda_1}^{\lambda=\lambda_2} \left( m \cdot dJ + \frac{e}{c} dF \right),$$

where

$$dF = \sum_{\mu} F_{\mu}^{(x)} \cdot dx_{\mu},$$

or of the integral

$$\int_{\lambda=\lambda_1}^{\lambda=\lambda_2} \left( \frac{m}{2} \sum_{\mu, \nu} J_{\mu\nu}^{(x)} \cdot \dot{x}_{\mu} \cdot \dot{x}_{\nu} \cdot dJ + \frac{e}{c} dF \right).$$

In view of the remarks of § 1 and of the investigation of the tracks of rays of light in the solar field which we shall make later, we shall use the second integral.

4. It has been remarked by Th. de Donder (2) that the equations to a geodesic of the dynamic manifold which are summarized in the formula

$$\delta \int_{\lambda=\lambda_1}^{\lambda=\lambda_2} dJ = 0$$

may also be written in the form

$$\frac{dx_a}{dJ} = \frac{\partial W}{\partial u_a}; \quad \frac{du_a}{dJ} = - \frac{\partial W}{\partial x_a}, \quad a = 1, 2, 3, 4,$$

where

$$u_a = \sum_{\mu} J_{\mu a}^{(x)} \cdot \dot{x}_{\mu}, \quad a = 1, 2, 3, 4$$

and

$$W = \sqrt{\sum_{\alpha, \beta} J_{\alpha\beta}^{(x)} \cdot u_{\alpha} \cdot u_{\beta}} \equiv 1.$$

5. Similarly it has been shown by W. Wilson (3) that the

equations of motions of a charged particle given above may be expressed in the form

$$\delta \int_{\lambda=\lambda_1}^{\lambda=\lambda_2} \sum_s \Pi_s \cdot dx_s = 0,$$

where 
$$\Pi_s = m \sum_t J_{st}^{(x)} \cdot \dot{x}_t + \frac{e}{c} F_s^{(x)}.$$

We now proceed to develop the ideas of the preceding sections along the lines suggested by the methods of Hamilton and Jacobi in classical mechanics.

6. The Lagrangian function  $L$  is defined by the equation

$$L = \frac{m}{2} \sum_{\alpha, \beta} J_{\alpha\beta}^{(x)} \cdot \dot{x}_\alpha \cdot \dot{x}_\beta + \frac{e}{c} \sum_\alpha F_\alpha^{(x)} \cdot \dot{x}_\alpha,$$

and is therefore an invariant. We take as our fundamental equation of motion the condition of the vanishing of the first variation of the invariant integral

$$\int_{\lambda=\lambda_1}^{\lambda=\lambda_2} L \cdot dJ.$$

This integral may be called the Action of the charged particle along the portion of the historical route which it pervades, defined by the inequalities

$$\lambda_1 \leq \lambda < \lambda_2.$$

From this "principle of least action" we deduce the Lagrangian equations

$$\frac{d}{dJ} \cdot \frac{\partial L}{\partial \dot{x}_\alpha} = \frac{\partial L}{\partial x_\alpha}, \quad \alpha = 1, 2, 3, 4,$$

which are equivalent to the equations of motion given in the preceding section. If

$$\frac{\partial L}{\partial x_\alpha} = 0,$$

$x_\alpha$  is called an "ignorable" coordinate (other coordinates being called "palpable" coordinates), and

$$\frac{\partial L}{\partial \dot{x}_\alpha} = \text{a constan}$$

is an immediate first integral of the equations of motion.



7. We now transform the Lagrangian equations by means of the Legendrian contact-transformation, obtained by writing

$$p_a^{(x)} = \frac{\partial L}{\partial \dot{x}_a}, \quad a=1, 2, 3, 4,$$

$$H = \sum_a p_a^{(x)} \cdot \dot{x}_a - L,$$

when the equations of motion assume the canonical form

$$\frac{\partial H}{\partial p_a^{(x)}} = \frac{d x_a}{d J}; \quad \frac{\partial H}{\partial x_a} = - \frac{d p_a^{(x)}}{d J};$$

since 
$$p_a^{(x)} = m \sum_{\beta} J_{a\beta}^{(x)} \cdot \dot{x}_{\beta} + \frac{e}{c} F_a^{(x)},$$

we deduce that

$$\sum_a p_a^{(x)} \cdot \dot{x}_a = L + \frac{m}{2} \sum_{\alpha\beta} J_{\alpha\beta}^{(x)} \cdot \dot{x}_{\alpha} \cdot \dot{x}_{\beta}$$

and 
$$\dot{x}_{\beta} = \frac{1}{m} \sum_a J_{a\beta}^{(x)} \cdot p_a^{(x)} - \frac{e}{mc} \sum_a J_{a\beta}^{(x)} F_a^{(x)}.$$

Hence

$$H = \frac{1}{2m} \sum_{\alpha,\beta} J_{\alpha\beta}^{(x)} \cdot p_{\alpha}^{(x)} \cdot p_{\beta}^{(x)} - \frac{e}{mc} \sum_{\alpha,\beta} J_{\alpha\beta}^{(x)} \cdot p_{\alpha}^{(x)} \cdot F_{\beta}^{(x)} + \frac{e^2}{2mc^2} \sum_{\alpha,\beta} J_{\alpha\beta}^{(x)} \cdot F_{\alpha}^{(x)} \cdot F_{\beta}^{(x)}.$$

8. In order to indicate that  $H$  is a function of  $x_a$  and  $p_a^{(x)}$  only, we shall write it in the form

$$H(x_1, x_2, x_3, x_4; p_1, p_2, p_3, p_4).$$

Now 
$$\frac{dH}{dJ} = \sum_a \left( \frac{\partial H}{\partial x_a} \cdot \frac{d x_a}{d J} + \frac{\partial H}{\partial p_a^{(x)}} \cdot \frac{d p_a^{(x)}}{d J} \right) \equiv 0,$$

$\therefore H = k$ , a constant.

Hence by Jacobi's Theorem, if

$$W(x_1, x_2, x_3, x_4; a_1, a_2, a_3, k) + a_4 = 0$$

be any complete integral of the partial differential equation of the first order and second degree,

$$H\left(x_1, x_2, x_3, x_4; \frac{\partial W}{\partial x_1}, \frac{\partial W}{\partial x_2}, \frac{\partial W}{\partial x_3}, \frac{\partial W}{\partial x_4}\right) = k,$$

the integrals of the canonical equations of motion are

$$\frac{\partial W}{\partial a_i} = b_i, \quad (i=1, 2, 3), \quad \frac{\partial W}{\partial k} = J - J_0,$$

and 
$$\frac{\partial W}{\partial x_i} = p_i^{(x)}, \quad (i=1, 2, 3, 4),$$

where  $b_i$  ( $i=1, 2, 3$ ) and  $J_0$  are arbitrary constants.

### *Planetary Motion.*

1. In the preceding exposition of the method of reducing particle dynamics according to the theory of relativity to a system of canonical equations, it has not been necessary to make any hypothesis regarding the actual form of the laws of gravitation and electromagnetism. We shall now discuss the problem of planetary motion according to the first three laws of gravitation mentioned on p. 86 of 'The Principle of Relativity,' by Whitehead, making the usual assumptions that the sun is at rest, and that perturbations due to the attraction of planets other than the one whose motion we consider may be neglected.

### *2. Einstein's Law.*

Let  $J^{(x)}$  denote the value of the symmetric determinant formed by the components of the fundamental tensor  $\|J_{\mu\nu}^{(x)}\|$ . Then the ten functions  $J_{\mu\nu}^{(x)}$ , ( $\mu, \nu=1, 2, 3, 4$ ) satisfy the ten partial differential equations of the second order,

$$\begin{aligned} \sum_{\rho} \left[ \frac{\partial}{\partial x^{\nu}} J_{\rho}^{[\mu\nu]}{}^{(x)} + J_{\rho}^{[\mu\nu]}{}^{(x)} \frac{\partial}{\partial x_{\rho}} \log \{ -J^{(x)} \}^{\frac{1}{2}} \right] \\ = \sum_{\rho, \sigma} J_{\rho} \left\{ \begin{matrix} \mu\sigma \\ \rho \end{matrix} \right\}^{(x)} \cdot J_{\sigma} \left\{ \begin{matrix} \nu\rho \\ \sigma \end{matrix} \right\}^{(x)} + \frac{\partial^2 \log \{ -J^{(x)} \}^{\frac{1}{2}}}{\partial x_{\mu} \partial x_{\nu}}, \end{aligned}$$

$\mu, \nu=1, 2, 3, 4.$

Since these equations are covariant, if  $\|J_{\mu\nu}^{(x)}\|$  is any set of ten functions satisfying them, and

$$x_{\mu} = x_{\mu}(\xi_1, \xi_2, \xi_3, \xi_4), \quad \mu=1, 2, 3, 4$$

is a set of four equations defining a transformation from the system " $x$ " to the system " $\xi$ ," then the ten functions

$$J_{\mu\nu}^{(\xi)} = \sum_{\alpha, \beta} J_{\alpha\beta}^{(x)} \frac{\partial x_{\alpha}}{\partial \xi_{\mu}} \frac{\partial x_{\beta}}{\partial \xi_{\nu}}, \quad \mu, \nu=1, 2, 3, 4$$

will also satisfy the equations, if  $\xi$  be substituted for  $x$ .

To obtain solutions of these equations appropriate to the solar field, many writers have assumed that the fundamental differential invariant of the dynamic manifold associated with the solar field is expressible in the form

$$dJ^2 = \epsilon^\nu \cdot c^2 \cdot dt^2 - \epsilon^\lambda \cdot dr^2 - \epsilon^\mu \cdot r^2 (d\theta^2 + \sin^2 \theta \cdot d\phi^2),$$

where  $(r, \theta, \phi)$  are spherical polar spatial coordinates,  $t$  is the temporal coordinate,  $\epsilon$  the base of Napierian logarithms, and  $\lambda, \mu, \nu$  functions of  $r$  only.

Thus the following writers have obtained solutions satisfying the above hypothesis and the supplementary conditions

$$\lim_{r \rightarrow \infty} (\lambda, \mu, \nu) = 0$$

together with other simplifying assumptions:—Einstein (4),  $[\lambda + 2\mu + \nu = 0, \text{ i.e. } J = -c^2 r^4 \sin^2 \theta]$ ; Dröste (6),  $[\lambda = 0]$ ; Schwarzschild (5),  $[\mu = 0]$ ; de Sitter, Hill and Jeffery (7) and (8),  $[\lambda = \mu]$ . Combridge (9) has shown that the general solution of Einstein's equations, subject to the condition that  $dJ^2$  is expressible in the above form, may be written

$$\epsilon^\lambda = \frac{1}{(1 - 2m/f)} \cdot \left(\frac{df}{dr}\right)^2, \quad \epsilon^\mu = \frac{f^2}{r^2}, \quad \epsilon^\nu = 1 - \frac{2m}{f},$$

where  $f$  is an arbitrary function of  $r$ , and  $m$  a constant of integration. To satisfy the supplementary conditions, we must have

$$\lim_{r \rightarrow \infty} f = r \quad \text{and} \quad \lim_{r \rightarrow \infty} \left(\frac{df}{dr}\right) = 1.$$

Finally, Forsyth (10) has shown that if  $dJ^2$  is expressible in the form

$$a \cdot dr^2 + b d\theta^2 + c d\phi^2 + d \cdot dt^2,$$

where  $a, b, c, d$  are functions of  $r, \theta, \phi$  only, and

$$\lim_{r \rightarrow \infty} (a, b, c, d) = (-1, -r^2, -r^2 \sin^2 \theta, c^2),$$

then we reach once more the solution

$$dJ^2 = \left(1 - \frac{2m}{r}\right) c^2 dt^2 - \frac{1}{\left(1 - \frac{2m}{r}\right)} dr^2 - r^2 (d\theta^2 + \sin^2 \theta \cdot d\phi^2).$$

$m$  is called the "gravitational radius" of the sun and equals  $\frac{\gamma M}{c^2}$ , where

$\gamma$  = the constant of gravitation,

$M$  = the mass of the sun,

$c$  = the velocity of light in *vacuo* where the gravitational field is zero.

The Lagrangian function is

$$I_1 = \frac{1}{2}\mu \left[ \left(1 - \frac{2m}{r}\right) \dot{c}^2 - \frac{\dot{r}^2}{\left(1 - \frac{2m}{r}\right)} - r^2 \dot{\theta}^2 - r^2 \sin^2 \theta \cdot \dot{\phi}^2 \right].$$

The ignorable coordinates  $\phi$  and  $t$  yield the equations

$$\mu r^2 \sin^2 \theta \cdot \dot{\phi} + p_\phi = 0,$$

$$\mu c^2 \left(1 - \frac{2m}{r}\right) \dot{t} = p_t,$$

where  $p_\theta$ ,  $p_\phi$ ,  $p_t$  are constants.

Let the axes be oriented so that  $p_\phi = 0$ . Then  $\mu r^2 \dot{\theta} + p_\theta = 0$ . Then the Hamiltonian equation is

$$\frac{1}{\left(1 - \frac{2m}{r}\right) c^2} \left(\frac{\partial W}{\partial t}\right)^2 + \left(1 - \frac{2m}{r}\right) \left(\frac{\partial W}{\partial r}\right)^2 - \frac{1}{r^2} \left(\frac{\partial W}{\partial \theta}\right)^2 = \eta,$$

and this possesses a complete integral in the form

$$W = p_\theta \cdot \theta + p_t \cdot t + z,$$

where  $z$  is a function of  $r$  only.

Put  $r \cdot u = 1$ , and we obtain the differential equation

$$u^4 (1 - 2m \cdot u) \left(\frac{dz}{du}\right)^2 = p_\theta^2 \cdot U,$$

where 
$$U = 2mu^3 - u^2 + \frac{2m\eta}{p_\theta^2} \cdot u + \frac{p_t^2 - \eta c^2}{p_\theta^2 c^2}.$$

Hence 
$$z = \pm \int \frac{p_\theta \cdot U^{\frac{1}{2}} \cdot du}{u^2 (1 - 2mu)}$$

and 
$$\frac{\partial W}{\partial p_\theta} = \theta + \frac{\partial z}{\partial p_\theta} = \theta \pm \int \frac{du}{U^{\frac{1}{2}}}.$$

Since  $\eta = \mu^2$ , this is the elliptic integral discussed by Forsyth (11).

Let 
$$U = 2m(u - \alpha)(u - \beta)(u - \gamma),$$

where 
$$\gamma < u < \beta < \alpha.$$

Then, it is shown in Forsyth's paper that  $\alpha, \beta, \gamma$ , the roots of the equation  $U=0$ , are real, distinct, and positive in the solar field.

Let 
$$p^2 = 2\mu(\alpha - \gamma) = \frac{\alpha - \gamma}{\alpha + \beta + \gamma}.$$

Measuring  $\theta$  from aphelion ( $u = \gamma$ ), we have, as in Greenhill's paper (12),

$$\sqrt{\frac{u - \gamma}{\beta - \gamma}} = \operatorname{sn} \frac{p\theta}{2} \left( \operatorname{mod} \sqrt{\frac{\beta - \gamma}{\alpha - \gamma}} \right),$$

where  $\operatorname{sn}$  is Jacobi's elliptic function defined by the equations

$$y = \int_0^x \frac{dx}{\sqrt{(1-x^2) \cdot (1-\kappa^2 x^2)}}, \quad |\kappa| < 1,$$

$$x = \operatorname{sn} y \pmod{\kappa}.$$

A discussion of the possible forms of the orbit has been given by Morton (13).

Let  $K$  denote the first complete elliptic integral modulus  $\sqrt{\frac{\beta - \gamma}{\alpha - \gamma}}$ , i. e. the real quarter period of  $\operatorname{sn} y$ , then the perihelionic advance in radians per revolution is

$$\psi = \frac{4K}{p} - 2\pi.$$

For all the inner planets this is approximately  $6\pi \frac{m^2}{h^2}$ , where  $\mu h + p\theta = 0$ . With the usual notation

$a$  = semi-axis major

and  $e$  = eccentricity of orbit.

By Forsyth's analysis  $h^2 \sim ma(1-e^2)$ , hence

$$\psi \sim \frac{6\pi\gamma M}{c^2 a(1-e^2)}.$$

### 3. Whitehead's First Law.

For the solar field this law can be expressed in the integral form

$$dJ^2 = (c^2 dt^2 - dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta \cdot d\phi^2) - \frac{2\gamma M}{c^2 r} (c^2 dt^2),$$

where

$$c(dt - dp) = dr,$$

whence the Lagrangian function is

$$L = \frac{1}{2}\mu \left[ \left(1 - \frac{2m}{r}\right) c^2 \dot{t}^2 - \left(1 + \frac{2m}{r}\right) \dot{r}^2 - r^2 \dot{\theta}^2 - r^2 \sin^2 \theta \cdot \dot{\phi}^2 \right. \\ \left. + \frac{4mc}{r} r \dot{t} \right].$$

The Lagrangian equations for the ignorable coordinates  $\phi, \gamma$  are

$$\left. \begin{aligned} \mu r^2 \sin^2 \theta \dot{\phi} + p_\phi &= 0, \\ \mu \left(1 - \frac{2m}{r}\right) c^2 \dot{t} + \mu \frac{2mc}{r} \dot{r} &= pt, \end{aligned} \right\}$$

where  $p_\phi$  and  $p_t$  are constants.

Choosing axes so that  $p_\phi = 0$ , we find that the Hamiltonian equation is

$$\frac{1}{c^2} \left(1 + \frac{2m}{r}\right) \left(\frac{\partial W}{\partial t}\right)^2 - \left(1 - \frac{2m}{r}\right) \left(\frac{\partial W}{\partial r}\right)^2 - \frac{1}{r^2} \left(\frac{\partial W}{\partial \theta}\right)^2 + \frac{4m}{rc} \left(\frac{\partial W}{\partial r}\right) \left(\frac{\partial W}{\partial t}\right) = \eta,$$

and  $\mu r^2 \dot{\theta} + p_\theta = 0$ ,

and this possesses a complete integral in the form

$$W = p_\theta \cdot \theta + p_t \cdot t + z,$$

where  $z$  is a function of  $r$  only.

Putting  $r \cdot u = 1$ , we obtain the equation

$$K \left(\frac{dz}{du}\right)^2 + 2L \left(\frac{dz}{du}\right) + M = 0,$$

where  $K = (1 - 2mu)u^4$ ;  $L = 2m \frac{p_t}{c} u^3$ ;

$$M = \left(p_\theta^2 u^2 - 2m \frac{p_t^2}{c^2} - \frac{p_t^2}{c^2} + \eta\right).$$

Hence 
$$\frac{dz}{du} = \frac{\frac{2mp_t u^3}{c} \pm p_\theta^2 u^2 U^{\frac{1}{2}}}{(1 - 2mu)u^4},$$

where 
$$U = 2mu^3 - u^2 + \frac{2m\eta}{p_\theta^2} u + \frac{p_t^2 - \eta c^2}{p_\theta^2 c^2},$$

the same cubic as that which occurred in the previous paragraph;

$$\therefore z = \int \frac{2mp_t du}{(1 - 2mu)cu} \pm \int \frac{p_\theta \cdot U^{\frac{1}{2}} \cdot du}{(1 - 2mu)u^2}$$

and 
$$\frac{\partial W}{\partial p_\theta} = \theta + \frac{\partial z}{\partial p_\theta} = \theta \pm \int \frac{du}{U^{\frac{1}{2}}}.$$

Hence we regain exactly the same equation to the form of the orbit as in the previous paragraph.

#### 4. *Whitehead's Second Law.*

In rectangular Cartesian axes this law may be written

$$\sum_{\lambda} \frac{1}{\omega_{\lambda}^2} \frac{\partial}{\partial x_{\lambda}} J[\mu\nu]^{(x)} = 0, \quad \mu, \nu = 1, 2, 3, 4,$$

where the constants  $\omega_{\lambda}$  are those which occur in the expression for the linear element of the metric manifold

$$ds^2 = \sum_{\lambda} \omega_{\lambda}^2 dx_{\lambda}^2.$$

Up to the present no researches on the equations have been published. We shall consider only those solutions which correspond to a steady gravitational field, i. e. for which  $J_{\mu\nu}^{(x)}$  is independent of  $x_4$ .

By writing  $\mu = \nu = 4$ , we obtain the equation

$$\frac{\partial^2 J_{44}^{(x)}}{\partial x_1^2} + \frac{\partial^2 J_{44}^{(x)}}{\partial x_2^2} + \frac{\partial^2 J_{44}^{(x)}}{\partial x_3^2} = 0.$$

The general solution of this equation, subject to the condition that  $J_{44}^{(x)}$  is a function of  $r$  only where

$$r = \sqrt{x_1^2 + x_2^2 + x_3^2},$$

$$\text{is} \quad J_{44}^{(x)} = c^2 \left( 1 - \frac{2m}{r} \right),$$

$c, m$  being constants of integration.

Assume that in spherical polar coordinates  $(r, \theta, \phi)$ ,  $dJ^2$  can be expressed in the form

$$dJ^2 = \left( 1 - \frac{2m}{r} \right) c^2 dt^2 - (1 + f(r) \cdot r^2) dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta \cdot d\phi^2 - g(r) r dr dt,$$

where  $f(r)$  and  $g(r)$  are functions of  $r$  only,

$$\begin{aligned} \text{Then} \quad J_{\mu\mu}^{(x)} &= -1 - x_{\mu}^2 \cdot f(r), & \mu &\neq 4, \\ J_{\mu\nu}^{(x)} &= -x_{\mu} x_{\nu} \cdot f(r), & \mu &\neq \nu; \mu, \nu \neq 4, \\ J_{\mu 4}^{(x)} &= -x_{\mu} \cdot g(r), & \mu &\neq 4. \end{aligned}$$

The ten equations which express Whitehead's Second Law

may be divided into three groups, obtained by setting

$$(1) \mu, \nu \neq 1, \quad \mu = \nu;$$

$$(2) \mu, \nu \neq 1, \quad \mu \neq \nu;$$

$$(3) \nu = 1, \quad \mu \neq 1.$$

The necessary and sufficient conditions for the satisfaction of groups (1) and (2) are respectively the equations

$$3f(r) + r \frac{df}{dr} = 0$$

$$\text{and} \quad 5 \frac{df}{dr} + r \frac{d^2f}{dr^2} = 0.$$

Hence  $f(r)$  reduces to a constant  $\lambda$ .

The third group of equations is satisfied identically, whatever the form of the function  $g(r)$ .

In order that the expression for  $dJ^2$  in polar coordinates should tend towards the form

$$c^2 dt^2 - dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta \cdot d\phi^2$$

as  $r$  tends to infinity,  $\lambda$  must be zero, and  $\lim_{r \rightarrow \infty} g(r)$  must be of higher order than  $\frac{1}{r}$ .

$$\text{Let} \quad r \cdot g(r) = R(r).$$

Taking as our expression for  $dJ^2$

$$\left(1 - \frac{2m}{r}\right) c^2 dt^2 - dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta \cdot d\phi^2 - R(r) dr \cdot dt,$$

we find as the Lagrangian function

$$L = \frac{1}{2} \mu \left[ \left(1 - \frac{2m}{r}\right) c^2 \dot{t}^2 - \dot{r}^2 - r^2 \dot{\theta}^2 - r^2 \sin^2 \theta \cdot \dot{\phi}^2 - R \dot{t} \right].$$

The Lagrangian equations for the ignorable coordinates  $r, \phi$  are

$$\mu r^2 \sin^2 \theta \cdot \dot{\phi} + p_\phi = 0,$$

$$\mu \left(1 - \frac{2m}{r}\right) c^2 \dot{t} - \frac{1}{2} \mu R \dot{r} = p_t,$$

where  $p_\phi$  and  $p_t$  are constants.



When the axes are oriented so that  $p_\phi = 0$ , the Hamiltonian equation is

$$(\pm\lambda + R^2) \left\{ 2 \left( \frac{\partial W}{\partial t} \right)^2 - 2\lambda \left( \frac{\partial W}{\partial r} \right)^2 - 2R \left( \frac{\partial W}{\partial r} \right) \left( \frac{\partial W}{\partial t} \right) \right\} - \frac{1}{r^2} \left( \frac{\partial W}{\partial \theta} \right)^2 = \eta,$$

and  $\mu r^2 \dot{\theta} + p_\theta = 0$ ,

where  $\lambda = c^2 \left( 1 - \frac{2m}{r} \right)$ .

This possesses a complete integral in the form

$$W = p_\theta \cdot \theta + p_t \cdot t + z,$$

where  $z$  is a function of  $r$  only.

Put  $r \cdot u = 1$ , and we obtain the equation

$$K \left( \frac{dz}{du} \right)^2 + 2L \left( \frac{dz}{du} \right) + M = 0,$$

where  $K = -2\lambda u^4$ ,

$$L = R \cdot p_t \cdot u^2,$$

and  $M = 2p_t^2 - (2\lambda + \frac{1}{2}R^2)(p_\theta^2 \cdot u^2 + \eta)$ .

Hence  $\frac{dz}{du} = \frac{-R p_t \pm c \sqrt{Q}}{-2\lambda u^2}$ ,

where  $Q = 4p_\theta^2 \cdot c^2 \left( 2mu^3 - u^2 - \frac{2m\eta}{p_\theta^2} u + \frac{p_t^2 - \eta c^2}{p_\theta^2 c^2} \right) \left( 1 - 2mu + \frac{R^2}{4c^2} \right)$ .

Proceeding as before, we find that

$$\theta = \pm \int \frac{2c \left( 1 - 2mu + \frac{R^2}{4c^2} \right)}{\sqrt{Q}} du.$$

Hence the necessary and sufficient condition that this should reduce to the same relation between  $u$  and  $\theta$  as that obtained in the two theories just discussed, is that

$$R = 2c \sqrt{2mu}.$$

This leads to  $g(r) = \frac{2c \sqrt{2m}}{r^{3/2}}$ ,

and hence satisfies the supplementary conditions, respecting the form of  $dJ^2$  as  $r$  tends to infinity.

*Deviation of Light Rays as in the Solar Field.*

It is shown in Murnaghan's paper (1) that the equations to the paths of rays of light in the solar field may be obtained by writing

$$\frac{1}{p_\theta}, \frac{1}{p_t} \rightarrow 0,$$

$$\frac{p_t}{p_\theta} \rightarrow \text{a finite quantity.}$$

The cubic  $U$  then takes the form

$$2mu^3 - u^2 - \alpha^2,$$

and in the practical application of the analysis to the solar field the three roots  $u_1, u_2$ , and  $u_3$  of the equation  $U=0$  are real, distinct, and satisfy the inequalities

$$u_1 < 0 < u < u_2 < u_3.$$

Hence, if

$$\frac{u - u_1}{u_2 - u_1} = \sin^2 \psi$$

and

$$\kappa^2 = \frac{u_2 - u_1}{u_3 - u_1},$$

the equation to the path of a ray of light on all three theories is

$$\theta = \int_0^u \frac{du}{U^{1/2}} = \sqrt{\frac{2}{m(u_3 - u_1)}} \int_{\sin^{-1} \sqrt{\frac{u_1}{u_3 - u_1}}}^{\psi} \frac{d\psi}{\sqrt{1 - \kappa^2 \sin^2 \psi}},$$

whence the approximate value of the total angular deviation suffered by a ray whose minimum distance from the sun is

$\frac{1}{u_2}$  is found to be  $4mu_2$  radians.

*Conclusion.*

It will be seen that the preceding method of treating the problem of central orbits according to relativistic theories has two merits to recommend it to the computer—it evades the tedious calculation of the Christoffel 3-index symbols, and it focusses attention at once on a differential equation, the solution of which furnishes the key to the whole problem. The principal results established in this paper by the use of this method are the following:—

(1) The equation of a planetary orbit has precisely the same form on Einstein's theory as on Whitehead's first

theory. In Whitehead's book, 'The Principle of Relativity,' it was shown that both theories yield the same expression for the perihelionic advance to a first approximation. This paper shows the exact equivalence of the formulæ.

(2) The equation of a planetary orbit on Whitehead's second theory involves an arbitrary function which can be chosen to yield the same equation as in the previous cases. This second theory has not been studied before.

Thus no observations of the forms of planetary orbit can discriminate between these three theories.

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XXXII. *Radioactive Disintegration Series.*—Part II.\* By W. P. WIDDOWSON, B.A., *Scholar of Christ Church, Oxford*, and A. S. RUSSELL, M.A., D.Sc., *Dr. Lee's Reader in Chemistry* †.

### § 1. *Introduction.*

IN Part I. it was shown that radioactive disintegration series are limited to four in number, the members of which have atomic weights given respectively by  $4n+3$ ,  $4n+2$ ,  $4n+1$ , and  $4n$ , where  $n$  is an integer. Reasons were given for supposing that the first of these is the actinium series, the second the uranium series, the third a hypothetical series the end-products of which may be isotopes of bismuth ( $a=209$ ) and of thallium ( $a=205$ ), and the fourth the thorium series. The present paper deals with the hypothetical series. It will show that experimental evidence is against the existence of this series in the possible form given in the earlier paper, and that theoretical considerations are not only consistent with this view, but render the existence of the series in any but an attenuated form unlikely.

### § 2. *Method of Investigation.*

The hypothetical series as postulated has a gaseous member of atomic number ( $z$ ) 86 and of atomic weight ( $a$ ) 221, which will for convenience be referred to as X. As an electro-scope can detect a much smaller amount of a gaseous radio-element than of a solid one, this member of the series appears to be the most suitable for examination. Its expected period, also, is a convenient one. This may be calculated from the periods of radon and thoron by the relation given in the paper cited, namely that the periods of radon, of X the hypothetical member considered, of thoron, and of acton are roughly in the ratio of  $80^3:80^2:80:1$ . An eightieth of radon's period is 69.3 minutes; eighty times thoron's is 72.0 minutes; the mean value of X's expected period is consequently 70.6 minutes. If this series existed along with the radium series in uranium minerals in such an amount that, for every hundred radon atoms breaking up per second, one or more atoms of X break up, then it is likely that the

\* Part I., A. S. Russell, *Phil. Mag.* xlv. p. 642 (1923).

† Communicated by the Authors.

series would have long ago been detected in the ordinary course of experiment. But if the equilibrium ratio were less than one per cent., X probably would not have been detected unless it had been specially looked for. It is clear, however, that if X exists and has a period of about an hour, its detection, even when the equilibrium ratio is as low as 1 to 1000, should not be very difficult. For if X and radon be completely removed from the mineral and then allowed to accumulate for an hour, the ratio of their relative activities is raised from  $\frac{1}{1000}$  to  $\frac{1}{8}$  because of the difference in their periods. If emanation of this composition be examined in an electroscope, it would be expected to show different properties from those of the two emanations in the proportions in which they naturally occur. It is quite possible, however, that X might exist and not have a period of the expected value. The closer the period is to that of radon the more difficult it would be to detect it. But if the period were much longer than that of radon it might easily have been overlooked, although, if it were looked for, it should be possible to detect it. Shortness of period would make detection easier provided the period is not so short that X has decayed considerably in the time of its transference from its parent-substance to the electroscope. The expulsion of  $\beta$ -particles instead of  $\alpha$ -particles by X would, other things being the same, make the detection of X much more difficult.

Failure to detect X may, then, be ascribed to one of four principal reasons :—

- (1) The parent of X may exist, but not in any of the preparations investigated.
- (2) X may exist in measurable amount, but its period is such that it is not likely to be detected without elaborate precautions.
- (3) X may have a suitable period and exist in uranium minerals, but in so small a proportion that in the unavoidable presence of radon it cannot be detected by ordinary means.
- (4) X does not exist.

In the present investigation we have looked for X only in the minerals pitchblende and thorianite and in a preparation of radium separated from pitchblende a few years ago. The first two of these are likely sources. Further, we have done only such experiments as are likely to reveal X if its period lies between four hours and four minutes.

§ 3. *Experimental work.*

4 grams of a pitchblende containing 25 per cent.  $U_3O_8$  was dissolved in nitric acid, 3.5 grams of barium chloride added, and the barium containing radium and the parent of X (an isotope of radium, if it exists) removed as sulphate. The sulphate was converted into barium carbonate by fusing with fusion mixture, and the carbonate dissolved in dilute hydrochloric acid to give a clear solution. When this solution is boiled the emanation is quantitatively expelled, as is well known. In the experiments to be described it is essential that this occurs, for otherwise the alteration in the ratio of the amounts of radon and of X by their growth for a known period of time after supposed complete expulsion, would not be that calculated from their known or supposed periods. In all experiments the emanation was transferred without loss through a drying apparatus to an air-tight emanation electroscope. Experiments to test if the emanation could be completely removed from the solutions used, and if the emanation electroscope was working properly, led to the following satisfactory results:—

Radium solution from pitchblende containing 25.4 per cent.  $U_3O_8$ . 1 scale-division of the instrument corresponds to 9.6, 9.5, 9.3, 9.5, and  $9.6 \times 10^{-8}$  mg. radium in different experiments.

Radium solution from thorianite containing 35.8 per cent.  $U_3O_8$ . 1 scale-division of the instrument corresponds to 9.5 and  $9.5 \times 10^{-8}$  mg. radium in two experiments.

*Experiment I.*—The solution of barium-radium chloride from pitchblende was made up to 45 c.c. 3 c.c. of this was placed in a flask, diluted with water, and the emanation expelled. A quarter of an hour later this operation was repeated. The flask was then sealed up for 2 days. At the end of this time the emanation was completely expelled into a gas-holder, and a few minutes later transferred to the electroscope through a tube containing calcium chloride to dry the gas, and through another to remove, as far as possible, solid disintegration products in the gas. Readings of the ionization produced in the electroscope were taken continuously every few minutes for three hours and then at longer intervals for the next hour. The maximum value, obtained by taking the mean of those obtained between  $2\frac{1}{2}$  and 3 hours after the transfer of the emanation into the electroscope, was taken as 100, and all values calculated on

X 2

this basis. A continuous curve was obtained when the values were plotted against the time. Four experiments of this kind were carried out. The mean values from the closely-agreeing curves at intervals of five and ten minutes are given in the column under I. in Table I.

TABLE I.

Time in minutes.	Pitchblende.				Radium.	Thorianite.
	I. Growth 2 days.	II. Growth 24 hours.	III. Growth 30 mins.	IV. Growth 1 min.	V. Growth 1 min.	VI. Growth 2 mins.
5 .....	59.8	62.6	62.8	68.0	68.5	—
10 .....	65.4	68.4	68.8	71.0	71.0	70.6
15 .....	69.4	71.8	71.8			
20 .....	72.2	74.0	74.0	76.0	76.0	74.2
25 .....	74.6	76.2	75.8			
30 .....	76.8	78.2	77.6	79.0	79.5	77.5
35 .....	79.0	79.8	79.4			
40 .....	81.0	81.2	81.0	82.0	82.4	81.0
45 .....	82.4	82.6	82.4			
50 .....	84.0	84.0	83.8	84.8	85.4	84.0
55 .....	85.4	85.4	85.2			
60 .....	86.8	86.8	86.6	87.6	88.0	87.0
70 .....	89.2	89.4	89.0			
80 .....	91.6	91.6	91.0	92.4	92.4	91.2
90 .....	93.8	93.6	93.0			
100 .....	95.4	95.2	94.8	96.3	96.0	95.2
110 .....	96.6	96.8	96.4			
120 .....	97.8	97.8	97.8	98	98	98
130 .....	98.6	98.8	98.4			
140 .....	99.2	99.2	99.2	99	99	99.5
150 .....	99.7	99.6	99.4			
160 .....	100	100	100	100	100	100

*Experiment II.*—42 c.c. of the solution used in experiment I. were placed in a flask and the emanation completely expelled. This operation was repeated, and the flask was then sealed up for  $2\frac{1}{2}$  hours. At the end of this time the emanation was removed, as before, from the flask into the electroscope. Measurements were made as in experiment I. Five experiments were carried out. The mean values of the relative ionizations produced are given in the column under II. in Table I.

*Experiment III.*—A solution of barium-radium chloride was separated from such a quantity of pitchblende that the quantity of radon which grew in it in half-an-hour gave an ionization in the electroscope that could be conveniently measured. The emanation was completely expelled, the flask sealed up for 30 minutes, and at the end of this time

the emanation which had grown was removed to the electro-scope. Measurements were made as in experiments I. and II. Four experiments were carried out. The mean values of the relative ionizations produced are given in the column under III. in Table I.

*Experiment IV.*—This was carried out in a similar way, but on a much larger quantity of active material. The emanation was allowed to grow, after complete expulsion, for 1 minute only and then drawn directly into the evacuated electro-scope. Three experiments were carried out. The mean values of the relative ionizations produced are given in the column under IV. in Table I.

*Experiment V.*—This experiment was carried out like experiment IV. on a solution of radium which had been extracted from pitchblende a few years ago. Six experiments were made.

*Experiment VI.*—This was carried out on a solution of barium-radium-mesothorium chloride extracted by us from a specimen of thorianite containing 35.8 per cent.  $U_3O_8$  and about 55 per cent.  $ThO_2$  in the following way:—The emanations were completely expelled. They were then allowed to grow for two minutes, at the end of which time they were removed to a gas-holder and kept there for 7 minutes to allow the thoron to decay to  $\frac{1}{250}$  of its initial value, and then drawn into the evacuated electro-scope. The first measurements were not accurate because the ionization was too great. Ten minutes after the transfer the effect of the thoron was negligible, and measurements thereafter were continued as before. Three experiments were carried out, the results of which are given in Table I. under VI.

#### § 4. Discussion of Results.

The results in the table may be divided into two groups: those in columns I. II. III. and VI., and those in columns IV. and V. It is seen that the results in the first three columns are very similar from 40 minutes to 160 minutes, but that the earlier values of I. are slightly smaller than the corresponding values of II. and III., which are very similar. If this difference is genuine it seems to be explained best by saying that X has a period of about 15 minutes and constitutes about 5 per cent. of the activity of radon and its products after they are five minutes in the electro-scope under the conditions of experiments II. and III. This, however, leads to difficulties. For if the ratio of the



activities of radon and of X in pitchblende is 1000, then, in experiment I., it may be calculated to be 302, and so X would be presumed undetectable. In experiment II. the ratio would be 18.6, which is approximately the ratio apparently detected. But in experiment III. the ratio would be as low as 5, and so X would contribute nearly four times more ionization than is found experimentally. In other words, the presence of a short-lived emanation would explain the differences between I. and II. but not the similarities of II. and III. On the other hand, the similarities would be consistent with the presence of an emanation with a period of 3 hours or more, but this product would not explain the differences between I. and II., which disappear after about 40 minutes. The difficulty cannot be resolved by considering in addition to X its possible active deposit, for although the nature and amount of the active deposit would be different in I., II., and III. in the emanations before they were transferred to the electroscope, this difference can hardly be operative inside the electroscope as the greater part of the deposit is prevented from entering by the glass wool and the drying agent. The difference under discussion is about three times the estimated experimental error.

The results of columns IV. and V. closely agree, but differ from those of the other columns. It would appear that a one-minute growth reveals something which the other experiments do not. The difference, we think, can best be explained as follows:—In experiments IV. and V. the emanation was transferred directly and in a few seconds from the vessel where it had grown to the electroscope. In experiments I., II., and III. the emanation was first collected in a gas-holder over water and then transferred to the electroscope, an operation taking about ten minutes. The effect of this difference in operations seems to make a difference of about six minutes to the times at which corresponding amounts of active deposit are formed in the emanation; the curves we obtained in IV. and V. are unmistakably those of II. and III. except for a shift of the time-axis by about six minutes. This may be seen also from Table I. If five minutes be added to the times given for the results of IV. and V., then the ionizations in II., III., IV. and V. are approximately the same.

An alternative explanation is that the effect is genuine and due to X. If so, X has an initial value of about 6 units, which falls to 2 in five minutes, to  $1\frac{1}{2}$  in fifteen minutes, and remains 1 till a hundred minutes. It is

therefore at least two products, one with a period of about three minutes and the second of two or three hours or so. The former product, if just detectable in an experiment in which the emanation accumulated for one minute, would not be detectable in experiments I., II., and III., so that the experimental results are consistent with the existence of this body.

Experiment IV. was again carried out with this difference, that the transfer of emanation was made as in experiments I., II., and III.; the results were approximately the same as those of I., II., and III. This is what would be expected on the first of the explanations offered; and also on the second, since during the ten minutes of the transfer the quick-changing emanation has decayed almost to zero, and the second product, presumed not a gas, is prevented from entering the electroscope.

Against the alternative explanation is this: that the ratio of parent and product in  $\alpha$ -particle activity cannot be lower than the reciprocal of the ratio of their periods. In this case the former ratio is, at most, 6 and the latter, at least, 20. This objection does not apply if the parent (in this case X) expels a  $\beta$ -particle, and its product an  $\alpha$ -particle.

To help to decide the matter experiment II. was repeated, except that on this occasion the accumulated emanation was transferred directly and quickly to the electroscope, as it had been in experiments IV. and V. The results now obtained were those of IV. and V. This shows conclusively that the difference effect is not due to an unknown radioactive body as suggested in the alternative explanation. It is probably due to the fact that in this method of transference a larger proportion of the active deposit of radon evaded the glass-wool and drying-apparatus and accompanied the radon into the electroscope than in the other method. Given a uniform method of transferring the emanation, exact timing of the moment the emanation reaches the electroscope, and a uniform method of measuring the ionization, we think the accuracy of our measurements is about 1 part in 200 when the mean of three values is taken.

In the experiments on the radium containing mesothorium separated from thorianite—experiment VI.—the effect of the thoron was enormous. Even after it had stood for seven minutes after its removal from its parent before being passed into the electroscope it was impossible to measure the combined emanations in the first five minutes. An emanation with a period of few minutes could not

therefore be detected in a source of thorium. In experiment VI., however, when the effect of thoron was spent, the rise-curve obtained was very similar to those obtained in experiments I., II., and III.

It seems, therefore, from these results that the six experiments appear to reveal no effects that cannot be explained without postulating the existence of a body X. They do not, however, exclude the possibilities that X might exist and have a period of the order of a minute, or that it might have a longer period and expel  $\beta$ -particles. It remains to discuss below what fraction of radon its concentration must be for it to exist and yet remain undetected in our experiments.

This fraction is obviously a function of X's supposed period, of the nature and intensity of X's radiation, and of the nature of X's active deposit. We propose to confine ourselves to cases in which it is supposed that X expels  $\alpha$ -particles of approximately the range of those from radon, that its period is between 4 minutes and 4 hours, and that the presence of an active deposit neither hinders nor helps the detection of X.

TABLE II.

Supposed period of X, in minutes.	Ionization due to X.	Ratio $\frac{X}{\text{Radon}}$ in		
		Exp. II. Growth $2\frac{1}{2}$ hours.	Exp. III. Growth 30 mins.	Exp. IV. Growth 1 min.
240	10	$\frac{1}{113}$	$\frac{1}{133}$	$\frac{1}{140}$
120	10	$\frac{1}{150}$	$\frac{1}{254}$	$\frac{1}{274}$
60	10	$\frac{1}{264}$	$\frac{1}{469}$	$\frac{1}{551}$
30	12	$\frac{1}{260}$	$\frac{1}{666}$	$\frac{1}{912}$
15	16	$\frac{1}{200}$	$\frac{1}{750}$	$\frac{1}{1350}$
15	10	—	—	$\frac{1}{2160}$
8	15	—	—	$\frac{1}{2600}$
4	20	—	—	$\frac{1}{2350}$

The information, calculated from our results, is given in Table II. In the first column are given various supposed

values of the period of X; in the second, values of ionizations contributed by X which would be detected from our results; and in the third, fourth, and fifth columns, the ratios of the activities of X to radon in a mineral which, in experiments II., III., and IV. respectively, would give the ionizations of column II. The ionizations of column II. are calculated taking the maximum point of radon's rise-curve as 100.

### § 5. Theoretical Considerations.

It has been pointed out by one of us\* that there is a close relation between the isotopes of radioactive elements and those of the inactive elements, it being possible to deduce in many cases the complexity of the latter from knowledge of the former. We propose here to discuss a converse problem: what light may be thrown on the possibility of the hypothetical series by present knowledge of inactive isotopes?

It may be deduced from Aston's collected results† that if an even element (*i. e.* an element of even atomic number) has an odd isotope (*i. e.* an isotope of odd mass-number), the latter is 3 or 1 units less than the principal even isotope. Indeed the rule seems to be, except for krypton, that when the element has two odd isotopes they are 3 and 1 units less, and when one isotope only, it is 3 units less. Neither of these rules applies to the light elements below sulphur.

Some results in illustration are given in Table III.

TABLE III.

Element.	Principal even isotope.	Odd isotopes.	
80. Mercury .....	202 §	199	—
54. Xenon.....	132	129	131
50. Tin .....	120	117	119
36. Krypton.....	84	—	83
34. Selenium .....	80	77	—

§ The likeliest value from Aston's results and atomic weight evidence.

It may also be deduced from Aston's results and from some (denoted by asterisks) given in the former of the papers by one of us cited, that one of the isotopes of an odd element is *usually* 5 units less than the principal even isotope of the element above it, if the latter be

\* A. S. Russell, 'Nature,' cxii. p. 588 (1923); Phil. Mag. xlvii. p. 1121 (1924).

† F. W. Aston, Phil. Mag. xlv. p. 934 (1923).

complex, and 1 or 3 units less, if it be simple. (A "simple" even element is one consisting *predominantly* of one isotope.) The rule is not absolute, but the number of exceptions are small and confined to the lighter elements.

Examples in illustration are given in Table IV.

TABLE IV.

Element <i>z</i> .	Nature.	Principal even isotope.	Element <i>z</i> - 1.	Mass- number.
82. Lead.....	Complex.	208†	81. Thallium .....	203*
80. Mercury .....	"	202	79. Gold .....	197*
54. Xenon .....	"	132	53. Iodine .....	127
50. Tin .....	"	120	49. Indium .....	115
36. Krypton .....	"	84	35. Bromine.....	79
34. Selenium .....	"	80	33. Arsenic .....	75
58. Cerium.....	Simple.	140*	57. Lanthanum ...	139*
42. Molybdenum ...	"	96*	41. Niobium.....	93*
38. Strontium .....	"	88	37. Rubidium .....	85
26. Iron .....	"	56	25. Manganese ...	55
16. Sulphur .....	"	32	15. Phosphorus ...	31

† Assumed. Very complex elements have as a rule principal even isotopes of mass-number  $4n$ . 208 is also the nearest even number to the atomic weight.

If both these considerations apply to even radio-active elements, we obtain the possibilities given in Table V.

TABLE V.

Element <i>z</i> .	Principal even isotope.	Possible odd isotopes.	Element <i>z</i> - 1.	Probable odd isotope.	Possible odd isotopes.
92. Uranium .....	238	235, 237	91. Protoactinium	233	231, 235
90. Thorium .....	232	229, 231	89. Actinium .....	227	225, 229
88. Radium .....	226	223, 225	87. — .....	221	219, 223
86. Radon .....	222	219, 221	85. — .....	217	215, 219
84. Polonium.....	210	207, 209	83. Bismuth.....	205	203, 207
82. Lead.....	208	205, 207	81. Thallium .....	203	201, 205

The figures in columns 3 and 5 are derived from those in column 2 from the considerations above, and those in column 6 from those in column 5, because an odd element may have two odd isotopes which differ by two units.

In compiling column 5 a difficulty has been to decide which of the even radio-elements are to be treated as complex, and which simple. Regarded as inactive elements, all but lead and possibly uranium are simple; regarded as radioactive elements, they are all complex. We have decided to assume in the first instance that each is complex.

The number of possibilities may now be reduced considerably by making the two following limiting assumptions:—

(1) Uranium is expected to have one odd isotope; radon and lead two; thorium, radium and polonium none\*. This excludes 237 from uranium, 229 and 231 from thorium, 223 and 225 from radium, and 207 and 209 from polonium as “probable” isotopes. (If they are “possible” they are likely relatively short-lived products.)

(2) Isobares of odd mass-number expelling the same type of radiation do not exist. (No odd isobares have yet been discovered among the inactive elements.)

This excludes 235 from protoactinium, 225 from radon, 219 from elements 87 and 85, 203, 205 and 207 from bismuth, and 205 from thallium. It also implies that successive radioactive changes in series of odd atomic number are confined to a succession of  $\alpha$ -particles and to the succession  $\alpha, \beta, \alpha, \beta$ .

The modified possibilities are given in Table VI. Since bismuth may not have isotopes of 203, 205 and 207†, it is given the value 209, which is, of course, the experimental value and that to be expected if polonium be regarded as a simple element. If bismuth has a second isotope, it can only be 211. These values are consequently added to the table under “probable” and “possible” respectively.

TABLE VI.

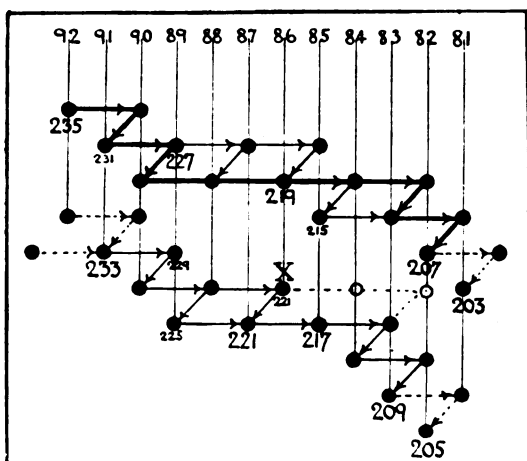
Element Z.	Probable odd isotopes.	Possible odd isotopes.
92. Uranium .....	235	—
91. Protoactinium ..	233	231
90. Thorium .....	—	—
89. Actinium .....	227	225 or 229
88. Radium .....	—	—
87. — .....	221	—
86. Radon .....	219	—
85. — .....	217	215
84. Polonium .....	—	—
83. Bismuth .....	209	211
82. Lead .....	205, 207	—
81. Thallium .....	203	—

If it be assumed that elements having mass-numbers greater than 209 are radioactive, two disintegration series

\* A. S. Russell, ‘Nature,’ cxii. p. 588 (1923); a fuller account is in course of publication.

† These end-products must be classed as  $\alpha$ -ray bodies, for if they were  $\beta$ -ray bodies the second assumption would be contravened.

may be drawn to embrace the above values, one embracing mass-numbers of the form  $4n+1$ , the other those of the form  $4n+3$ . Neither of these is unique, various possibilities being allowed by the data. Each series is drawn to pass through the "probable" mass-numbers (printed in large type), through the "possible" mass-numbers (printed in smaller type) and through any mass-number which is not inconsistent with the data given in the above table (these are not printed). The series are shown in the figure.



It is seen that one of the possibilities of the upper series is part or the whole of the actinium series \* which is the alternative that does not pass through elements 87 and 85. This is shown in thicker type. A second possibility—namely, that which passes from  $z=89, a=227$  to  $z=87, a=223$  and rejoins the actinium series either at  $z=88, a=223$  or  $z=86, a=219$ —is unlikely since the expulsion of  $\alpha$ -particles by actinium ( $z=89, a=227$ ) has not been observed, but it appears possible. This second possibility would form a branch of the actinium series, and if such exists the branching ratio at actinium must be very small. The third possibility is that a branch occurs at actinium A ( $z=84, a=215$ ). There is nothing to be said against this, as the possibility that a small proportion of  $\beta$ -particles accompanies the  $\alpha$ -particles of actinium A has not been

\* See Part I., *loc. cit.* p. 646.

tested experimentally, and would indeed be a very difficult thing to substantiate if it exists.

The lower series differs from the actinium series in that it keeps more particularly to elements of odd atomic number. There are again three alternative routes, but all pass through  $z=87, a=221$  and  $z=85, a=217$ ; and one of them passes through all of the elements of odd atomic number in its course. The relation of these to the hypothetical series of Part I. of this paper is illustrated in the figure. The hypothetical series is identical with one of the possibilities as far as the point marked X; it then continues along the dotted line and joins the series again at  $z=83, a=213$ , and continues with it to  $z=83, a=209$  (bismuth).

If the lower series exists its long-lived members are  $z=91, a=233$ , the apparent head of the series;  $z=87, a=221$ ;  $z=85, a=217$ , with  $z=83, a=209$  as a possible end-product. It should consequently be looked for in minerals containing tantalum, but it need not exist in minerals containing thorium or uranium. Uranium might have an isotope 237 which by an  $\alpha$ - and a  $\beta$ -change is transformed into the head of this series, but if so it is more complex than is to be expected; the element  $z=93, a=237$  is also a possible parent, but it, like its homologues, the missing elements 75 and 43, is probably unstable. These possibilities are indicated in the figure by dotted lines. However the series goes in its earlier stages, it ought not to pass through the element X in the way anticipated in Part I. of this paper. If it goes through X, X emits  $\beta$ -not  $\alpha$ -particles and is transformed into a body about whose period nothing is known. This anticipation is consistent with our failure to find X experimentally, because, as is well known, the ionization contributed by a  $\beta$ -particle relative to that contributed by an  $\alpha$ -particle is small. It may be argued, however, that this lower series is an unlikely one for the following reason. It is to be expected on general grounds that series whose members have odd atomic weights pass through the odd elements, and those whose members have even atomic weights through the even elements. The upper series in the figure may run either through even or odd elements, and it is known experimentally that it avoids the elements 85 and 87 and passes through elements 86, 84, and 82. The possibility of passing through even elements appears to be partly excluded from the lower series, and if it be not possible for a series to pass through the elements 87 and 85, the series (if it ever starts) may come to an end at the product which



would otherwise have been transformed into an isotope of element 87.

In the form the series are given in Table VI. and the figure, element 87 is simple with a mass-number of 221. Element 85 may also be regarded as simple with a mass-number of 217 until its possible second isotope 215, a branch product of actinium A, is discovered.

### *Summary.*

(1) A search has been made in pitchblende, in thorianite, and in a preparation of radium for an isotope of radon, thoron, and acton expelling  $\alpha$ -particles with an anticipated period of 70 minutes. This was unsuccessful.

(2) It is concluded either that, if this hypothetical emanation exists and expels  $\alpha$ -particles, its period must be greater than 4 hours or less than 4 minutes; or that, if its period lies between the above limits, the number of atoms breaking up per second must be less than a value which varies between  $\frac{1}{140}$  for the higher limit of period and  $\frac{1}{2350}$  for the lower, of that of a member of the radium series in pitchblende or in thorianite.

(3) It is to be anticipated theoretically that there are only three out of four possible radioactive series which have members of atomic number 86 emitting  $\alpha$ -particles. The fourth, if it exists, should arise from an isotope of proto-actinium having an atomic weight of 233, pass through the missing elements 87 and 85, and end in bismuth.

(4) The principal isotopes of elements 91, 85, and 87 are calculated to be 233, 221, and 217 respectively. Elements 85 and 87 are probably simple.

We wish to thank the Government Grant Committee of the Royal Society for providing us with the instruments and materials employed in this work.

Dr. Lee's Laboratory,  
Christ Church, Oxford,  
March 1924.

XXXIII. *Scattering of Light by very big Colloidal Particles.*  
 By WAS. SHOULEJKIN, *Professor of Physics, Higher  
 Technical School, Moscow* \*.

• 1. *Introduction.*

**T**HE theory of light scattering developed by Lord Rayleigh †, and perfectly confirmed by a series of precise experiments, relates to the case of light falling on very small particles whose diameter is many times smaller than the wave-length of light.

In this case only do the relations stated by Lord Rayleigh allow us to define the brightness of light, radiated by a particle at some angle to its previous direction, as well as the polarization of the scattered light. Such particles as, for example, the molecules of gas, whose light-scattering has been thoroughly studied by Abbot and Fowl ‡ and J. Cabannes §.

But if one turns from molecules to colloidal particles—to colloidal solutions of resins, oil emulsions, etc.—the picture changes drastically: one notices already by sight that the scattering of light is here unsymmetrical towards the planes perpendicular to the incident rays. Light is brightest along directions not far away from the previous one, and is least bright in the opposite direction, whereas Rayleigh's formula gives a symmetrical distribution ||.

If one studies the polarization of light scattered at different angles to the previous direction, it appears that the maximum of polarization corresponds to azimuth considerably greater than  $90^\circ$ , and here also polarization is incomplete.

All this shows that the laws of scattering of light by big particles vary greatly from those of the scattering by particles which are small in relation to the wave-length, and this difference is the greater, the coarser the particles.

The problem of scattering of light by particles of any dimension has been studied in general by G. Mie ¶, taking into account also the absorption of light by the particles

\* Communicated to the Scientific Institution of Moscow, November 21, 1922.

† Lord Rayleigh, *Phil. Mag.* (4) xli. (1871); (5) xii. (1881); (5) xvii. (1899).

‡ Abbot & Fowl, *Astrophys. Journ.* xxxiv. p. 203 (1911); xxxviii. p. 392 (1913).

§ J. Cabannes, *Annales de Physique*, xxv. p. 1 (1920).

|| The experimental measurements have been made originally by Ramanathan, *Phil. Mag.* xlv. p. 543 (1923).

¶ G. Mie, *Ann. d. Phys.* xxv. p. 377 (1908).

whose electrical conduction is not zero. But with a growth in the size of the particles the difficulties of calculation grow also rapidly, being at last rather serious.

Therefore Mie's studies were pursued only so far as to deal with particles a third of the size of the wave-length.

The present article fills up the gap between the small particles and *those of any size* (to the limit of infinitely big ones in comparison with the wave-length). In solving this problem we shall use the methods of the elaborate studies of Mie, but we shall limit our case to particles which have the ideal properties of a dielectric.

## 2. *The Theory of Mie.*

A flat wave falls on a spherical particle placed at the pole of a system of coordinates  $(r, \vartheta, \phi)$ . By an integration of Maxwell's equations for the field inside and outside of the particle, and solving them together with the equations for a flat wave, Mie obtains expressions for the amplitudes of waves radiated by the particle in all directions and superposed on a flat wave.

As the common integral of Maxwell's equations includes a series of partial solutions, the whole radiation of the particle can be divided into an infinite number of partial waves. If  $\nu$  be the number of partial waves and  $x$  be put equal to  $\frac{2\pi \cdot r}{\lambda}$ , where  $r$  is the distance of the pole and  $\lambda$  the wave-length of light in the surrounding solvent, the components of the amplitudes of the electrical vectors can be expressed in accordance with G. Mie as follows:—

$$\left. \begin{aligned} E_r &= \sum_{\nu=1}^{\infty} a_{\nu} \cdot i \cdot \frac{K_{\nu}(-x)}{x^2} \cdot P_{\nu}; \\ E_{\vartheta} &= \sum_{\nu=1}^{\infty} \left[ \frac{a_{\nu} \cdot i}{\nu(\nu+1)} \cdot \frac{K_{\nu}'(-x)}{x} \cdot \frac{\partial P_{\nu}}{\partial \vartheta} \right. \\ &\quad \left. + \frac{p_{\nu}}{\nu(\nu+1)} \cdot \frac{K_{\nu}(-x)}{x \cdot \sin \vartheta} \cdot \frac{\partial \mathfrak{P}_{\nu}}{\partial \phi} \right]; \\ E_{\phi} &= \sum_{\nu=1}^{\infty} \left[ \frac{a_{\nu} \cdot i}{\nu(\nu+1)} \cdot \frac{K_{\nu}'(-x)}{x \cdot \sin \vartheta} \cdot \frac{\partial P_{\nu}}{\partial \phi} \right. \\ &\quad \left. + \frac{p_{\nu}}{\nu(\nu+1)} \cdot \frac{K_{\nu}(-x)}{x} \cdot \frac{\partial \mathfrak{P}_{\nu}}{\partial \vartheta} \right]. \end{aligned} \right\} \quad (1)$$

Here  $K_{\nu}(-x)$  (and  $K_{\nu}'(-x)$ ) is a function (and its derivative) entering into the integral of Maxwell's equations

which depends upon  $r$ ;  $P$ , and  $\mathfrak{P}$ , are functions of  $\mathfrak{S}$  and  $\phi$ . The magnetic components  $M_r$ ,  $M_\theta$ , and  $M_\phi$  are expressed similarly.

The functions  $a_\nu$  and  $p_\nu$  entering into all expressions are defined by border conditions; these are complex functions, depending upon the wave-length, the radius of the particle, and the index of refraction of the material of the particle in relation to the outer medium  $m'$ .

The relations are considerably simplified if one supposes that the point where the field of light is studied is as far from the particle as  $r$ , a distance very great in comparison with its radius  $\rho$ .

In accomplishing corresponding modifications, G. Mie passes from amplitudes of vectors to the values of intensity of light radiated by the particle in all directions. The intensity of the incident light is taken as a unit. For the definition of the polarization of the scattered light Mie investigates two of its components: (1) the radiation  $I_I$  whose electrical oscillations are perpendicular to the plane of sight, and (2) the radiation  $I_{II}$  whose electrical oscillations are in the plane of sight itself (but, indeed, also perpendicular to the ray of sight).

If the scattered ray investigated makes an angle  $(\pi - \gamma)$  with the ray falling on the particle, then the intensities  $I_I$  and  $I_{II}$  will be expressed according to Mie as:

$$\left. \begin{aligned} I_I &= \frac{\lambda^2}{4\pi^2 r^2} \left| \sum_{\nu=1}^{\infty} \left\{ \frac{a_\nu}{\nu(\nu+1)} \Pi_\nu + \frac{p_\nu}{\nu(\nu+1)} (\Pi_\nu' \cos \gamma - \Pi_\nu' \sin^2 \gamma) \right\} \right|^2; \\ I_{II} &= \frac{\lambda^2}{4\pi^2 r^2} \left| \sum_{\nu=1}^{\infty} \left\{ \frac{a_\nu}{\nu(\nu+1)} (\Pi_\nu \cos \gamma - \Pi_\nu' \sin^2 \gamma) + \frac{p_\nu}{\nu(\nu+1)} \Pi_\nu \right\} \right|^2. \end{aligned} \right\} \quad (2)$$

The sign  $|^2$  shows that the quadrate of the absolute value of the complex in the parenthesis is taken.  $\Pi_\nu$  are spherical functions,  $\Pi_\nu'$  their first derivatives on  $\cos \gamma$ .

The summation  $I_I + I_{II}$  gives the full intensity of the rays scattered under the angle  $\gamma$ , and the difference  $I_I - I_{II}$  is the surplus of polarized light. If the difference is positive, the light is polarized so that the electrical oscillations are perpendicular to the plane of sight; if it is negative, the electrical oscillations are in the plane of sight. The number  $\nu$  of the partial waves which can be considered sufficient for

calculations depends upon the size of the particle in relation to the wave-length.

We shall calculate four cases :

$$(a) \operatorname{Lim}_{\lambda} \frac{\rho}{\lambda} = 0; \quad (b) \frac{2\pi\rho}{\lambda} = 1; \quad (c) \frac{2\pi\rho}{\lambda} = 3;$$

$$\text{and finally} \quad (d) \operatorname{Lim}_{\lambda} \frac{\rho}{\lambda} = \infty.$$

Let us take as a colloid a substance with an index in relation to the medium  $m' = 1.32$ . This corresponds to an emulsion of paraffin oil in water or to drops of condensed vapour in air. The results obtained can also, with some modifications, be applied to the case  $m' = \frac{1}{1.32}$ , corresponding to bubbles of gas suspended in water.

### 3. *The very small Rayleigh's Particles.*

In this case the radiation consists in the first partial wave:  $\nu = 1$ . Besides  $p_1 = 0$  in equations (2), of the two complex functions  $a_1$  and  $p_1$  only  $a_1$  appears where

$$a_1 = 2\alpha^3 \frac{m'^2 - 1}{m'^2 + 2},$$

where  $\alpha$  is an abbreviation for  $\frac{2\pi\rho}{\lambda}$ .

Again,  $\Pi_1 = 1$  and  $\Pi_1' = 0$ . On putting these values into (2), we have :

$$I_I = \frac{\lambda^2}{4\pi^2 r^2} \left| \frac{a_1}{2} \right|^2; \quad I_{II} = \frac{\lambda^2}{4\pi^2 r^2} \left| \frac{a_1}{2} \cos \gamma \right|^2.$$

And finally:

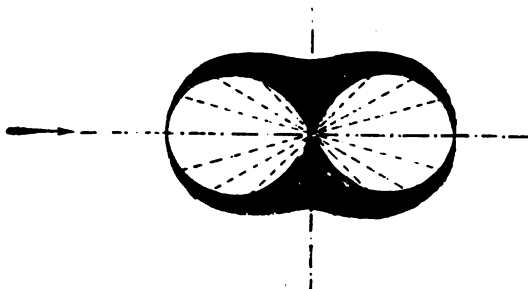
$$I_I + I_{II} = \frac{16\pi^4 \cdot \rho^6}{\lambda^4 r^2} \left[ \frac{m'^2 - 1}{m'^2 + 2} \right]^2 (1 + \cos^2 \gamma);$$

$$I_I - I_{II} = \frac{16\pi^4 \cdot \rho^6}{\lambda^4 r^2} \left[ \frac{m'^2 - 1}{m'^2 + 2} \right]^2 (1 - \cos^2 \gamma).$$

This is evidently Rayleigh's law of scattering. On plotting out graphically the intensity of scattered light along polar coordinates in some scale on radii-vectores, we get the curves of fig. 1. The outer curve represents the full brightness of the dispersed light, and the parts of the vectors between the

outer and the inner one (in the shaded part) the admixture of polarized light. The maximum of polarization corresponds

Fig. 1.



to an angle of  $90^\circ$  to the incident rays; the polarization is here complete, and the electrical oscillations are perpendicular to the plane of sight.

4. *Particles of a Diameter about a third of the Wave-length of Light.*

Let us suppose  $\frac{2\pi\rho}{\lambda} = 1$ .

In this case, as Mie has done, one has to take into consideration the first ( $\nu=1$ ) and the second ( $\nu=2$ ) partial wave. But out of all the complex values  $a_1$ ,  $p_1$ ,  $a_2$ , and  $p_2$ , the last one ( $p_2$ ) can be still left out of account. The remaining coefficients are equal to the following values, if one drops the common multiplicator  $e^{-i}$  which does not influence the result:

$$\begin{array}{ll} a_1 = 0.156 - i.0.324 & \Pi_1 = 1. \\ p_1 = -0.025 + i.0.040 & \text{with } \Pi_1' = 0. \\ a_2 = -0.017 + i.0.027 & \Pi_2 = 3 \cos \gamma. \\ & \Pi_2' = 3. \end{array}$$

In simplifying the calculations we drop in the formula (2) the multiplier  $\frac{\lambda^2}{4\pi^2 r^2}$  before the parenthesis, because at

present we want to find the law of the distribution of energy around the particle, and not the absolute brightness of light.

Therefore, out of the modified equations (2) we determine the values  $j_I$  and  $j_{II}$ , proportional to  $I_I$  and to  $I_{II}$ .

Equations ready for calculations have the following aspect :

$$j_I = \left| \frac{a_1}{2} + \frac{a_2 + p_1}{2} \cos \gamma \right|^2 ;$$

$$j_{II} = \left| \frac{a_1}{2} \cos \gamma + \frac{a_2}{2} \cos 2\gamma + p_1 \right|^2 .$$

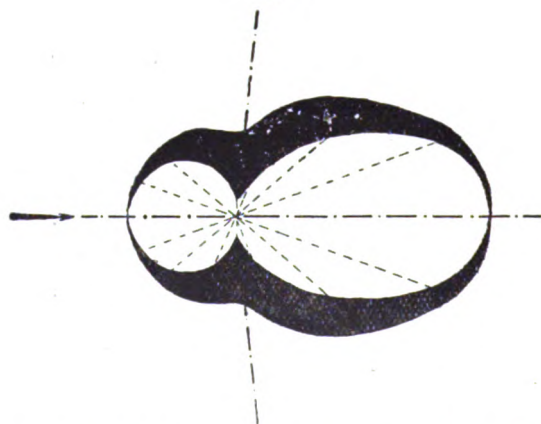
The results of the calculations are given in Table I.

TABLE I.

Angle $\gamma$ ...	0°.	20°.	40°.	60°.	90°.	120°.	140°.	160°.	180°.
The full brightness (relat.).	0.0390	0.0387	0.0380	0.0360	0.0325	0.0462	0.0667	0.0875	0.0925
The polarized light.	0	0.0020	0.0070	0.0155	0.0297	0.0327	0.0212	0.0060	0
Percentage of polarized light.	0	5.2	18.5	43	91	71	32	6.8	0

The law of radiation is graphically represented in fig. 2. Here, as in fig. 1, the radii-vectores of the outer curve

Fig. 2.



express the full brightness of light, and their parts in the shaded surface the admixture of polarized light, where the plane of polarization is the same (that of Rayleigh) as in fig. 1. The maximum of polarization is here removed from

90° towards the direction of the falling rays. The polarization is *everywhere complete*. The whole curve is more symmetrical; its left part is contracted, its right part is more developed than that of Rayleigh's in fig. 1.

5. *Particles whose Diameter is approximately equal to the Wave-length.*

Let us suppose  $\frac{2\pi\rho}{\lambda} = 3$ .

With this size of a particle one has to consider several partial waves, which rather complicates calculations. After a determination of the amplitudes of several partial waves, we found that it is possible to ignore waves from the 4th degree upwards ( $\nu=4$ ). Therefore one has to summarize three separate electrical and three separate magnetic oscillations for  $\nu=1$ ,  $\nu=2$ , and  $\nu=3$ . The coefficients  $a_1$ ,  $p_1$ ;  $a_2$ ,  $p_2$ ;  $a_3$ ,  $p_3$  in the formula (2) determined by border conditions were found to be :

$$\begin{aligned} a_1 &= -1.7 + i.1.25; & p_1 &= -0.224 - i.3.32. \\ a_2 &= 2.54 - i.1.27; & p_2 &= -2.64 + i.1.48. \\ a_3 &= 1.51 - i.0.12; & p_3 &= 0.676 + i.0.029. \end{aligned}$$

Further :

$$\begin{aligned} \Pi_1 &= 1; & \Pi_2 &= 3 \cos \gamma; & \Pi_3 &= 7.5 \cos^2 \gamma - 1.5. \\ \Pi_1 &= 0; & \Pi_2 &= 3; & \Pi_3 &= 15 \cos \gamma. \end{aligned}$$

Instead of  $I_I$  and  $I_{II}$  let us calculate, as in the former section, the values  $j_I$  and  $j_{II}$ , proportional to them. After some simplifications we obtain the following expressions for  $j_I$  and  $j_{II}$  :

$$\begin{aligned} j_I &= |Q_I \cos^3 \gamma + R_I \cos^2 \gamma + S_I \cos \gamma + T_I \cos 2\gamma + U_I|^2; \\ j_{II} &= |Q_{II} \cos^3 \gamma + R_{II} \cos^2 \gamma + S_{II} \cos \gamma + T_{II} \cos 2\gamma + U_{II}|^2. \end{aligned}$$

Here :

$$Q_I = \frac{22.5}{12} p_3; \quad Q_{II} = \frac{22.5}{12} a_3.$$

$$R_I = \frac{7.5}{12} a_3; \quad R_{II} = \frac{7.5}{12} p_3.$$

$$S_I = \frac{p_1 + a_2}{2} - \frac{16.5}{12} p_3; \quad S_{II} = \frac{a_1 + p_2}{2} - \frac{16.5}{12} a_3.$$

$$T_I = \frac{p_2}{2}; \quad T_{II} = \frac{a_2}{2}.$$

$$U_I = \frac{a_1}{2} - \frac{a_3}{8}; \quad U_{II} = \frac{p_1}{2} - \frac{p_3}{8}.$$



The numerical values for those ten complex coefficients are given in Table II.

TABLE II.

	I.	II.
Q.....	1.27 + i.0.054	-2.83 - i.0.225
R.....	-0.945 - i.0.750	0.424 + i.0.018
S.....	0.230 - i.2.33	-0.085 + i.1.525
T.....	-1.32 + i.0.740	1.27 - i.0.630
U.....	-0.660 + i.0.640	-0.197 - i.1.664

The calculation of  $j_I$  and  $j_{II}$  for nine different azimuths gives the full (relative) brightness of dispersed light  $j_I + j_{II}$  as well as the admixture of polarized light  $j_I - j_{II}$  (see Table III.).

TABLE III.

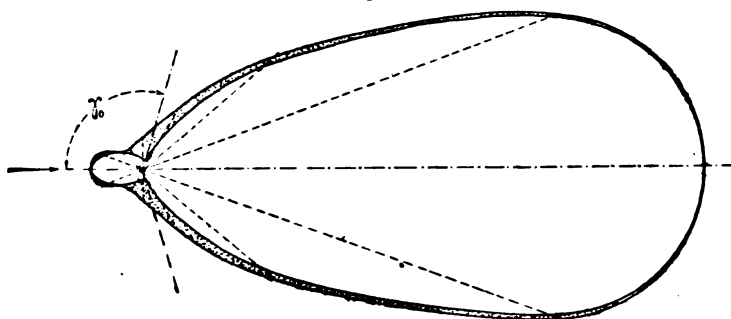
Angle $\gamma$ ...	0°.	20°.	40°.	60°.	90°.	120°.	140°.	160°.	180°.
Full brightness (relative).	6.0	5.03	3.06	2.70	3.56	7.94	19.7	50.5	64.4
Admixture of polarized light.	0	+0.25	-0.13	-1.06	-2.68	-3.6	-1.45	-0.5	0
Percentage of polarized light.	0	+5	-4.2	-38.1	-75	-45	-7.4	-1	0

The sign (—) before almost every number of the third line shows that the plane of polarization is turned at an angle of 90° in relation to that of Rayleigh, and the electrical oscillations are in the plane of sight.

Fig. 3 shows the law of radiation represented, as before, in a polar system of coordinates. It is evident that there is little in common between scattering of light by small (§ 3) and big particles, and that the curve of radiation is sharply deformed, developing in the direction of incident rays.

Even the polarization is here, as we have seen, quite in a different plane. Rayleigh's polarization (§ 3) has been preserved only for very small azimuths (where the surface between the outer and inner curve is *shaded*; but where this surface is dotted the plane of polarization is perpendicular to that of Rayleigh). The maximum of polarization is still more displaced from  $90^\circ$  than in case § 4, and the degree of polarization even at this optimal angle is still less complete.

Fig. 3.



What is the physical meaning of this change in the character of scattering? What does such a deformation of the curve of radiation, such a displacement of the maximum of polarization and even of the plane of polarization, signify? We shall endeavour to solve these questions in § 6, investigating the last of the possible cases with very big particles, for which the relation  $\frac{\rho}{\lambda}$  tends towards infinity.

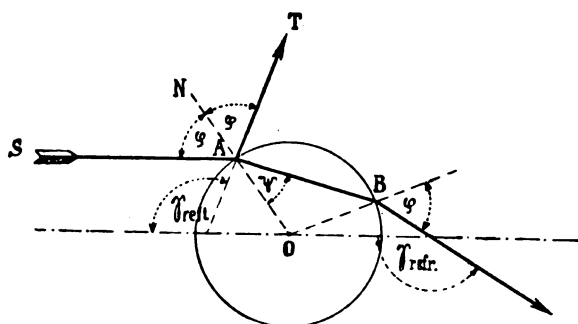
## 6. The biggest possible Particles.

In the case of such big particles, for which  $\text{Lim } \frac{\rho}{\lambda} = \infty$ , we shall not proceed with the calculations used above, but we shall use quite different methods.

It is easy to conjecture that such big spherical dielectric globes will simply refract and reflect rays falling upon them, and that the brightness of the reflected and refracted rays radiated by these balls in all directions can be calculated on a basis of common propositions.

Fig 4 shows the details of this case. Let one of the parallel rays (SA), shining upon the globe, fall upon it in the point A, forming with the normal AN an angle  $\phi$ . A part of the light-energy will be reflected at an angle SAT to the ray SA, so that evidently  $\text{SAT} = 2\phi$ .

Fig. 4.



Therefore for reflected rays  $\gamma = 2\phi$ . The brightness of the ray reflected at such an azimuth can be found from the relation

$$\left. \begin{aligned} I_{\text{refl}} &= I_{\text{inc.}} \cdot \Phi \cdot \cos \phi, \\ \text{where there is an abbreviation,} \\ \Phi &= \frac{1 \sin^2 (\phi - \psi)}{2 \sin^2 (\phi + \psi)} \left[ 1 + \frac{\cos^2 (\phi + \psi)}{\cos^2 (\phi - \psi)} \right]^2 \end{aligned} \right\} \cdot (3)$$

The admixture of polarized light is

$$\left. \begin{aligned} (I_{\text{refl.}})_{\text{polar.}} &= I_{\text{inc.}} \cdot \Phi' \cdot \cos \phi, \\ \text{where} \\ \Phi' &= \frac{1 \sin^2 (\phi - \psi)}{2 \sin^2 (\phi + \psi)} \left[ 1 - \frac{\cos^2 (\phi + \psi)}{\cos^2 (\phi - \psi)} \right]^2 \end{aligned} \right\} \cdot (3')$$

The plane of polarization will be, evidently, perpendicular to that of Rayleigh, because electrical oscillations will be in the plane of sight.

At an angle  $\phi_0 = \arctang(m')$  the reflected ray will be completely polarized. Therefore a ray with an azimuth  $\gamma_0 = 2\phi_0 = 2 \arctang(m')$  will be completely polarized. In our case, where  $m' = 1.32$  the value of  $\gamma_0$  will be  $\gamma_0 = 105^\circ 40'$ .

The calculations of brightness of the reflected light are given in Table IV., where the brightness of the incident light is taken as a unit.

TABLE IV.

Angle $\gamma$ .....	10°.	20°.	30°.	40°.	60°.	90°.
The full brightness of the reflected light.	0·017	0·017	0·018	0·0182	0·0169	0·0182
Admixture of polarized light (in a reflected ray).	0·000	0·0010	0·0020	0·0036	0·0077	0·0180

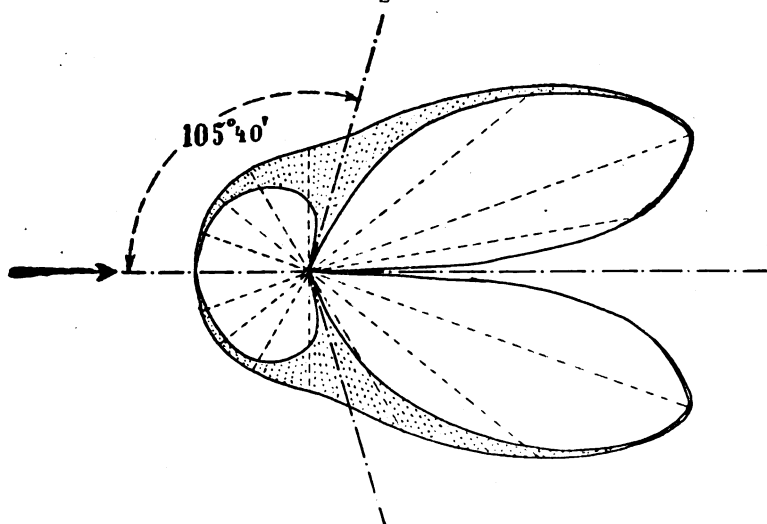
120°.	140°.	150°.	160°.	170°.	179° 40'.
0·0287	0·0441	0·0539	0·0600	0·0506	0·0030
0·0285	0·0425	0·0510	0·0190	0·0076	0·000

Therefore it is evident that if  $\gamma=0$ ,

$$I_{\text{refl.}} = \left( \frac{m' - 1}{m' + 1} \right)^2 = 0·017 \cdot I_{\text{inc.}},$$

and that if  $\gamma=180^\circ$ ,  $I_{\text{refl.}}=0$  (because  $\cos \phi=0$ ).

Fig. 5.



The same law of reflexion at different azimuths is represented graphically in fig. 5.

But the full energy of "scattering" by a spherical globe is evidently composed of two parts: one of them, the energy of the wave reflected from the surface, we have already taken into account. It remains to calculate the energy of rays which have penetrated through an absolutely transparent dielectric globe and are refracted at its surface.

We see in fig 4 that a refracted ray will come out of the ball under the same angle  $\phi$  to the normal line in the point of exit (B) at which it previously fell upon the surface of the ball in the point A. Therefore the brightness of the reappearing ray will be found from the relation

$$I_{\text{refr.}} = I_{\text{inc.}} \cdot (1 - \Phi)^2 \cdot \cos \phi,$$

where  $\Phi$  has its previous significance. The azimuth of this ray is easily found from the geometrical relations; it will be

$$\gamma_{\text{refr.}} = 180^\circ - 2(\phi - \psi).$$

The values for  $I_{\text{refr.}}$  calculated for a series of angles  $\gamma_{\text{refr.}}$  (corresponding to values of the angle  $\phi = 5^\circ, 10^\circ, 15^\circ$ , etc.) are represented in Table V.

TABLE V.

Angle $\gamma_{\text{refr.}}$ ...	177° 40'.	175° 20'.	172° 40'.	170° 0'.	164° 40'.	155° 0'.
Brightness of light which passes through the ball.	0.967	0.950	0.933	0.907	0.836	0.709

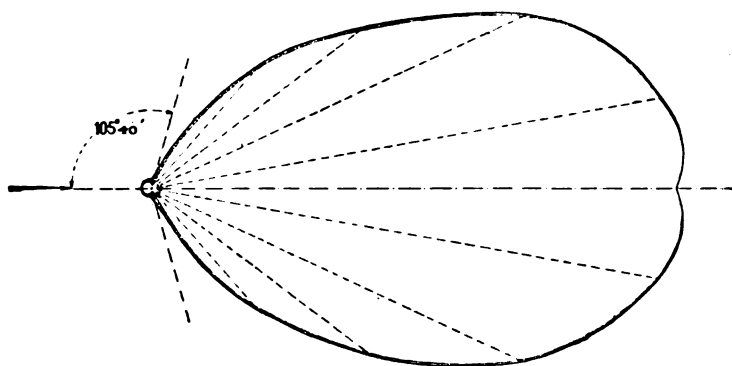
142° 0'.	131° 0'.	124° 20'.	116° 20'.	108° 0'.	98° 40'.
0.450	0.260	0.162	0.075	0.015	0.000

The polarization of these rays can be determined from Table IV. For a precise calculation of the "scattering" of energy, one has to take into account the secondary, tertiary, etc. refractions of rays inside the globe, but this feebly influences the final result, and we omit them. In summarizing the energies of rays ( $\alpha$ ) reflected by the surface of

the ball and (b) those which pass through it, we find the final law of scattering graphically represented in fig. 6.

We can see that this fig. 6 resembles fig. 3, which has been obtained on the proposition of the theory of scattering of light for particles whose diameter is approximately equal to the wave-length ( $\frac{2\pi\rho}{\lambda}=3$ ). And this likeness is not occasional or external, but *very deep* and of an inner origin.

Fig. 6.



If one considers the polarization of rays in both cases, in order to prove the correctness of the above said, the plane of polarization just at the position of the maximum of polarization is the same in both cases (in the latter case the polarization will be also incomplete, even at an optimal angle of  $105^{\circ} 40'$ , because upon a completely-polarized wave of fig. 5 another not fully-polarized wave, which has passed through the globe, is superposed).

The law of scattering itself, found in § 5, has now a clear physical meaning: the greater development of the right part of the curve with a growth of the diameter of the particles is caused by an *emerging refracted wave* which has passed through a dielectric ball. The maximum of polarization, corresponding in Rayleigh's particles to an angle of  $90^{\circ}$ , is *striving for an optimal angle  $\gamma_0$ , which is equal to a double angle  $\phi_0$  of a complete polarization of the reflexion* (the tangent of the latter is equal to the index of refraction  $m'$ ).

#### Conclusion.

1. The distribution of scattered energy of light around a radiating particle of a turbid medium (dielectric in an ideal state) is subject to Lord Rayleigh's formula, if diameters of

the particles  $2\rho$  are included in the limit  $0 < 2\rho < \frac{1}{3}\lambda$ . At an angle  $\gamma_0 = 90^\circ$  the scattered light is completely polarized (the electrical oscillations are perpendicular to the plane of vision).

2. Already at  $2\rho \cong \frac{\lambda}{3}$  one notices a definite asymmetry of dispersion, so that along the direction of incident rays the brightness of the scattered light is 2.5 times greater than in the opposite direction (these calculations have been made for a relative index of refraction  $m' = 1.32$ ). The angle of maximal polarization is displaced from  $90^\circ$  in the direction of incident rays. The polarization is everywhere incomplete, but in the same plane as in point 1.

3. With diameters bigger than  $2\rho \cong \lambda$ , the asymmetry is still greater; with  $2\rho \cong \lambda$  and with  $m' = 1.32$  the brightness of light dispersed in the direction of incident rays is approximately 11 times greater than the brightness in the opposite direction. The maximum of polarization is displaced still more from the angle  $90^\circ$ , tending in the limit to the angle  $\gamma_0 = 2 \arctan(m')$ . The plane of polarization itself completely changes with such dimensions of the particles; it gets perpendicular to the plane of polarization of Rayleigh's particles, *i. e.* electrical oscillations are in the plane of sight.

4. This plane of polarization as well as the character of distribution of the dispersed energy, *from these dimensions of particles upwards, does not change any more* until just the greatest dimensions of particles which can be studied by common methods *applying the laws of refraction and reflexion of light*. The greater and still greater development of the curve in the direction of incident rays is due to the wave which *has passed through* the dielectric globe.

5. In limits with dimensions of particles infinitely greater than the length of the wave, the brightness of light scattered in the direction of incident rays is 52 times greater than the brightness in the opposite direction (if  $m' = 1.32$ ). The angle of maximal polarization is in this case equal to  $105^\circ 40'$ .

6. There is, therefore, a smooth continuous change from scattering of light to its reflexion and refraction.

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XXXIV. *Notes on the Constitution of Spectra.* By W. M. HICKS, *Emeritus Professor of Physics, University of Sheffield.*

I. *In re the Oun.*

THE opinion has been expressed that the discovery of isotopes has invalidated the evidence for the existence of the *oun* and the part it plays in the constitution of sequence terms. This is, however, based on a misconception of the evidence. When it is remembered that the first discovery of the *oun* effect was led up to by the general belief at the time that the doublet and triplet separations depended in some way on the squares of the atomic weight, such a misconception is perhaps natural. If the problem had been considered after the publication of Aston's researches on isotopes, it would probably have been tested on the basis of squares of atomic numbers. In that case the result would have been nugatory† and the discovery of the *oun* effect would have been left for some future investigator.

The magnitude of all doublet, triplet, and satellite separations is a secondary effect depending on definite changes in the denominator of the function  $N/D^2$  which gives the value of the terms of a sequence. Thus in a doublet series, the limits are given by  $N/D^2$  and  $N/(D-\Delta)^2$ , so that the separation of the two series is  $\nu = N/(D-\Delta)^2 - N/D^2$ . If we wish to determine how the separation ( $\nu$ ) depends on any natural quantity, it is the  $\Delta$  and not the  $\nu$  which we have to study. A consideration of these  $\Delta$  showed, that if  $w$  denote (atom. wt.)/100 then in all cases where the series were known the  $\Delta$  (or  $\Delta_1$ ,  $\Delta_2$  in triplets) were integral multiples of a quantity  $= (90.445 \pm .005)w^2$ , within observational errors spectroscopic or chemical. In fact, with the more accurate data of to-day any alteration of a multiple by unity entirely upsets the relation. That it is possible to do this with elements whose atomic weights range from 23 (Na) to over 200 (Hg, Tl, Ra) is in itself a remarkable result. But it is then found that the satellite separations in *d* and *f* sequences, as well as the enhanced doublets in group II. (ionized atoms) also depend in a similar way on multiples of the same *oun*, and indeed that other effects, not further dealt with in this note, depend on *oun* values.

This dependence of all the various separations on the *oun* opens up a possibility of an independent and purely spectral determination of the *oun* values, especially in cases where

\* Communicated by the Author.

† See 'Analysis of Spectra,' p. 149.



triplet series occur or where the successive spectra of multiply ionized atoms are known\*. To do this with confidence accurate spectroscopic measures are required, especially for D and F satellites where observation errors are multiplied by large factors in the corresponding  $\Delta$ . Ultimately we may hope to obtain a large number of our values thus independently obtained, and then it will be possible to consider directly their dependence on the atomic weight.

Meanwhile, on the evidence as it stands at present we can hardly escape from the conclusion that as an experimental fact the  $\sigma$  is proportional to the square of the atomic weight, that is to a quantity which, in at least a large number of cases, corresponds to no physical entity. Possibly a way out of the difficulty may be indicated by the following considerations. To fix ideas take the case of an element with two isotopes A, B. It is usual to *explain* the observed atomic weight as the statistical mean of the two isotopes occurring in their respective numbers. The ratio in their numbers appears as a quite definite one, the same from whatever source the element tested has been taken. Why, in the building up—or degrading—of successive elements, do we find that for each particular one the isotopes are always in this ratio? If the numbers were equal we might take it as due to pure chance, but this explanation is not here tenable. There must be some cause which, in the building up of an element, settles in a precise way the probability of the entrance of each isotope; and this cause must depend in some way on the constitution of the element itself. Does this cause also affect the different energy levels which in any sequence produce the doublet and triplet separations? If so, the  $\sigma$  depends on this quality directly, and only in a secondary sense on the observed atomic weight, because this latter also depends on it.

## II. The Aluminium $\sigma$ .

The recent remarkable work of Paschen† on the spectra of the singly and doubly ionized atom of aluminium enables

\* *E. g.* in Cd with very accurate measures:—

	Cd.		Cd <sup>+</sup> .
$\Delta_1$ .	23105.83 = $203 \times 113.819$ .	$\Delta$ .	27348 = $240 \times 113.94$ .
$\Delta_2$ .	10870.33 = $91 \times 113.959$ .	$\sigma$ .	4314 = $38 \times 113.53$ .
$\Delta_1 + \Delta_2$ .	33476.16 = $294 \times 113.864$ .		
$\sigma_1 + \sigma_2$ .	3303 = $29 \times 113.89$ .		

The satellite in Cd<sup>+</sup>(4314) depends on two ultra-violet lines with considerable possible errors in wave number. It agrees with 113.864 within possible errors.

† *Ann. der Phys.* lxxi. pp. 142, 537 (1923).

us to illustrate the exactness of the own relation in this element very fully. It must be noted that values of the  $\Delta$  obtained with enhanced spectra are specially accurate, since on account of the  $4N, 9N$ , etc., relation, their percentage uncertainties are very much diminished. In the present case in addition the observations themselves are of the first order of accuracy. For the neutral atom the own relations for the doublet separations and the satellite separations for  $D(2)$  and  $D(3)$  are very fully obeyed \*, but as the own values for all the early elements in any periodic group are small, their evidential value for proving the reality of the relation was not great. The new spectra, however, afford increased data with striking agreement.

The various data from the three spectra are here given. Paschen's values for the terms in Al II, Al III are all affected with the same unknown error, but it is small and the effect on our deduced values is inappreciable. We shall use the value of  $\delta$  (4 ouns) as given in the 'Analysis' and determined from the doublet separation of Al I. In the case of triplets the values for the sum of the separations are also given, because in the majority of elements there is a small "triplet modification" as between  $\nu_1$  and  $\nu_2$ , although  $\nu_1 + \nu_2$  is normal. This modification, however, is almost negligible in the early elements of a group.

$$\delta = 4\delta_1 = 26.5465 \pm .0045.$$

		Sep.	$\Delta$ .	
Al I Doublet.	$p(1).....$	$112.038 \pm .010$	$1752.07 \pm .30$	$66\delta$
	$d(2).....$	1.33	110	$4\frac{1}{2}\delta = 112.8$
	$d(3).....$	4.49	823	$31\delta = 822.9$
Al II Triplets.	$p(1).....$	125.5	1075	$40\frac{1}{2}\delta = 1075.1$
		61.8	529	$20\delta = 530.9$
		187.3	1604	$60\frac{1}{2}\delta = 1606.0$
	$d(2).....$	2.16	53.5	$2\delta = 53.1$
		1.12	27.8	$\delta = 26.5$
		3.28	81.3	$3\delta = 79.6$
	$f(3).....$	2.81	194.0	$7\frac{1}{2}\delta = 192.5$
		2.09	143.7	$5\frac{1}{2}\delta = 146.0$
		4.90	337.7	$12\frac{3}{4}\delta = 338.5$
	$F(3) \dots$	47.53	3286.2	$123\frac{3}{4}\delta = 3285.1$
Al. III Doublet.	$p(2).....$	238.00	1606.2	$60\frac{1}{2}\delta = 1606.0$
	$p(3).....$	80.30	1592.0	$60\delta = 1592.7$

It will be noticed that the  $\Delta$  for  $\nu_1 + \nu_2$  in Al II and  $\nu$  in

\* 'Analysis' pp. 128, 136, misprints on p. 136 here corrected.

Al III have the same value  $60\frac{1}{2}\delta$ , although the  $\nu_1 + \nu$  and  $\nu$ —187.3 and 238—are quite different. This illustrates the fact that the essential quantity to study is the  $\Delta$  and not the separation observed.

### III. The Spectrum of Manganese.

The  $S'''$  (2, 3) and  $D'''$  (2, 3, 4) sets were allocated by Kayser and Runge in 1894. Extensions up to  $m=7$  were given in my 'Analysis of Spectra.' Catalan\* has since given a very full discussion of the different series of this element. His work has brought to light a number of new facts and has been the occasion of extraordinarily interesting extensions by Sommerfeld of his descriptive theory of internal quantum numbers and by Landé of his empirical method of pre-determining the Zeeman patterns, verified experimentally by Back. This note, however, has no reference to these questions, but considers only a few minor points relating to series arrangements. It is followed by a short excursus on the theory of displacement, illustrated by the higher orders of these series.

For  $P_{123}'''$  (2) Catalan gives  $\lambda=15263$ ,  $n=6550$  and supports it by two suggested combinations  $n_n=27280.20$ ,  $27444.65$  as  $p_11-p_k2$ ,  $p_21-p_k2$ . As  $p_21-p_11=173.6$  the separation of these,  $164.45$ , is too large for different  $k$  and too small for same  $k$ . The following are suggested as preferable (measures by Fritsch):—

	I.	$\lambda$ .	$n$ .	
$p_11-p_22$	1,	3667.758	27257.79	
$p_11-p_22$	3,	3664.779	27279.95	
$p_11-p_12$	4,	3660.549	27311.47	} 173.80
$p_21-p_22$	3,	3641.579	27453.75	

These give for  $P(2)$  the set, in wave-number:—

6585.50	
	31.52
6553.98	
	22.16
6531.82	

The separations are in the same ratio as in  $P(1)$  and of the order of magnitude to be expected. They also support Catalan's allocation of  $\lambda=15263$  as a mean value of  $P_{123}'''(2)$ . His proposed set for  $P(3)$  give separations also in about the same ratio and of suitable magnitude. But with these two sets for  $P(2, 3)$  his  $\lambda=6315$  for  $P(4)$  is doubtful, as indeed

\* Trans. Roy. Soc. 223 A. p. 127.

he indicates. Its denominator would be 4.8376 as compared with 1.6305, 2.8047, 3.8360 for the others, and too small to be in step. We should expect one about 4.8516 corresponding to about  $\lambda = 6300$ .

In the  $S'''$  we agree up to  $m=5$ , whilst Catalan gives a slightly different set for  $m=6$  and none for  $m=7$ . The equation calculated from  $m=2, 3, 4$  exactly reproduces the wave number for  $m=5$ . The formula may therefore be considered as very reliable. For  $m=6$  it deviates very largely from Catalan's allocation, less from mine, but still outside observation errors. For  $m=6, 7$  the calculated values fall in a region containing a large number of displaced lines, and are considered below in note IV. In  $D'''$  again Catalan gives up to  $m=5$  only. We differ slightly for  $m=5$ , but again we come into a region of displacement also considered in note IV. The equations, with  $N=109678.7$ , are

$$S_1''', 41254.06 - N/\{m + 1.378714 - .067251/m\}^2$$

$$D_1''', 41254.06 - N/\{m + .904297 - .049476/m\}^2,$$

$S$  being determined from the first three lines and  $D$  from the  $S(\infty)$  and the first two lines. The  $\nu$  separations show an anomalous ratio of 1.34, or say 4:3, instead of being greater than 2. They seem analogous to those of O, S, in group VI. with ratios 1.8, 1.6, although Se in the same group gives 2.5. The  $D$  sequence is also unusual in that the coefficient of  $1/m$  is negative, but the outstanding interest of the  $D$  series is that the sequence *genus d* comprises five *species* in place of the three hitherto known. These species are analogous to those of the triplets hitherto recognized, in being formed by successive negative displacements. In the newly found single groups of multiplets on the contrary, they are formed by successive positive displacements.

The presence of triplets in an element of group VII., where according to Rydberg's rule we should expect doublets, is an anomaly for which Catalan's explanation is probably correct\*. But another anomaly also occurs in connexion with the series which in other elements constitute a singlet system associated with the triplet. For the singlet systems to be expected we apparently get triplets. But if this is really the case, we have a new fact in spectral constitution, the evidence for which calls for careful examination. As a contribution towards this, the series arrangements are

\* But see Sommerfeld, *Ann. d. Phys.* lxxiii. p. 217 (1924), *Phil. Mag.* S. 6. Vol. 48. No. 284. Aug. 1924. Z

here discussed rather more fully than would otherwise be necessary.

For the singlet representatives he finds triplet systems in about the correct position and composed of lines of correct spectral behaviour. In addition there is another triplet system, parallel to this, in which the first members of each order are separated by 10967.75 from the corresponding line of the other. As this second series has separations 14.22, 8.70, in the ratio 5:3, we shall take it that its limit term belongs to a  $d$  sequence, that of the first being of the  $p$  type.

There can be little doubt but that the allocation of  $s'1 - \rho_2'''1$  is correct and from this,  $s'1$  can be calculated ( $=59959.40$ ). Regarding the first series as a split representative of a true  $S'$ , the first line gives with the above  $s'1$  the limit  $\rho_12$  as 24189.39. But if it is not, the series must be treated independently, and the formula calculated from the first three lines. The result is to give a limit 216 larger. The formula calculated with the supposed  $\rho_2$  limit and the first two orders gives for the third ( $m=3$ ) a line in error by 53A. This might seem decisive against the hypothesis, were it not that in these typical singlets, the first line is in general greatly out of step with the others, and a formula calculated with it unsuitable. It is found better to determine the formula from the next three lines, or as here, where the limit is given, from that and the second and third orders. The two formulæ are then, on the two hypotheses,

$$S_1^n, \quad n=24405.17 - N/\{m + .484377 - .134311/m\}^2$$

$$S_1', \quad n=24189.39 - N/\{m + .578576 - .294684/m\}^2,$$

where  $S^n$  refers to that of an independent narrow triplet, and  $S'$  to that of a "singlet" system.

The first equation gives lines for  $m=4, 5$  at  $n=18868.53$  and 20722.76. The former is close to two observed lines ( $3n$ ) 18866.95 and ( $2n$ ) 18870.10. Moreover, a line at ( $2$ ) 29838.44 is separated from 18870 by the shift 10968.34, only .6 greater than that between the two parallel series. Further, as this is the shift between the first lines of each order, it is supporting evidence that 18870 is  $S_1(4)$  or close to it. But it does not show triplets with lines  $\nu_1, \nu_2$  ahead. Indeed, the other line 18866.95 is the centre of a congeries of triplets. There is clear evidence of considerable displacement and linkage effects in both regions round 18870 and 29838.

The second formula gives for  $m=1$  a line at  $\lambda 2361A$ , quite impossible for the observed 2794A. For singlets,

especially with a large  $\alpha$ , as here, we often find considerable discrepancies between observation and calculation for the first line, but in this case it is very excessive. On the other hand, the calculated lines for  $m=4, 5$  are found with approximate triplets. The calculated have  $n=18784.95, 20589.40$ . As the matter is important from its bearing on general theory, the data are more closely discussed in the next note.

The annexed table gives the own relations for different series. The values of the satellite separations of the normal  $D'''$  series vary so greatly as given by different observers, that displacement in both terms or some unknown effect is clearly present and it is impossible to assign definite values. The separations for the first three orders of P are given, in which it should be remembered that those for P(2) are measured on the  $p1-p2$  combinations and are consequently very accurate. The values for the "singlet" series and the dependent multiplets will depend on the limit adopted— $S^*$  or  $S'$ . That of  $S^*$  may be in excess by an error  $<10$ . The  $S'$  limit is definite within about  $\pm 1$ . Both are given, those depending on  $S'$  in italics. Further, the values for the sum of the separations are also given, as owing to the "triplet modification" effect it is this to which the multiple law is applicable.

		$\delta = 109.233 + .36d\nu.$		$d\nu < .01.$	
		sep.	$\Delta.$	$x.$	$x\delta.$
$p'''1$	173.628		3420.32	31½	3413.5
	129.272		2532.90	23½	2539.7
	<b>302.900</b>		<b>5953.22 + 19.5dν</b>	54½	<b>(109.233 + .36dν)</b>
$p'''2$	31.52		3164	29,	3167.7
	22.16		2219	20½	2211.9
	<b>53.68</b>		<b>5383.6 + 100dν</b>	49½	<b>5379.7</b>
$p'''3$	9.52		2448	22½	2457.7
	7.39		1896	17½	1884.3
	<b>16.91</b>		<b>4344 + 257dν</b>	39½	<b>4342.0</b>
$p$	44.11	1913.2	17½, 1911.5	<i>1938.8</i>	<i>17½, 1938.8</i>
	35.87	1551.9	14½, 1556.6	<i>1572.7</i>	<i>14½, 1583.9</i>
	<b>79.98</b>	<b>3465.1 + 43dν - .212ξ</b>	31½, <b>3468.1</b>	<b>3511.5</b>	<i>32½, 3522.7</i>
$p'$	14.222	353.88	3½, 355.0	<i>357.13</i>	<i>3½, 355.0</i>
	8.703	216.6	2, 218.46	<i>218.42</i>	<i>2, 218.46</i>
	<b>22.925</b>	<b>570.50 + 25dν - .025ξ</b>	5½, <b>573.46</b>	<b>575.55</b>	<i>5½, 573.46</i>

Separations with three decimal places are the means of several good measures. The  $\Delta$  are slightly affected by errors in the limit, with possible changes in  $N$ , as well as in the

separations. In  $p'''2$  an exact multiple requires a  $d\nu = -0.39$ . As  $\nu$  is measured on lines about 3660 Å, this requires  $d\lambda = 0.005$ . In  $p'''3$  an exact multiple requires also  $d\lambda = 0.005$ . In  $p'$  it is curious that both hypotheses give close multiples for  $\nu_1$ , but the crucial values for  $\nu_1 + \nu_2$  definitely exclude the  $S'$  hypothesis and allow the  $S''$  provided the limit error is about  $-8$  (see IV. p. 342). The  $d'$  numbers as they stand exclude both, although the multiple law is clearly indicated. The valid deduction is that as we are dealing with new types of sequences (the Zeeman patterns \* are quite different from those of our known triplets in group II.) we are not justified in assuming *a priori* that rules based on the others are rigorously applicable to these new ones. What the discussion really shows is that the old rules are still applicable rigorously to the main triplet terms and probably with some modification to the new "singlet" triplets. *E.g.*, where the old rule applies to the sum, here, in the narrow triplets it applies to the first, and not to the second, but this question cannot be decided at present. From this point of view it may be interesting to place on record the data determined from the first two of Catalan's multiplets. In both these we have double sets depending on the same  $p', d'$  limits with common second terms, say  $\phi_1, \phi_2 \dots$ . In the first,  $\phi_1 = N/(2.9\dots)^2$  with small separations suggesting analogy with  $D''$ . The separations adopted are the means of all the observed, and the  $\Delta$  are discussed for  $\sigma_1, \sigma_1 + \sigma_2 \dots$ . In the second  $\phi_2 = N/(1.59\dots)^2$ , the separations are large and are adopted from the measures of the  $p' - \phi_2$  multiplet as they are more reliable than those from  $d' - \phi_2$ . This term  $\phi_2$  is important, acting as the limit term in the remaining multiplets.

$\phi_1$	$\sigma_1$	4.76	535.17	5, 546.1	547.4	5, 546.1
	$\sigma_1 + \sigma_2$	8.29	930.1	$8\frac{1}{2}$ , 928.5	953.6	$8\frac{1}{2}$ , 955.7
	$\sigma_1 \dots \sigma_3$	10.83	1212.9	11, 1201.6	1245.9	$11\frac{1}{2}$ , 1256.1
	$\sigma_1 \dots \sigma_4$	12.40	1391.28	$11\frac{1}{2}$ , 1283.5	1426.4	13, 1420
			+112d $\nu$		+115d $\nu$	
$\phi$	$\sigma_1$	229.67	4264+18d $\nu$	39, 4260.1	4297	$39\frac{1}{2}$ , 4287.4
	$\sigma_2$	169.53	3170	29, 3167.8	3193	$29\frac{1}{2}$ , 3195.1
	$\sigma_3$	116.95	2197	20, 2184.7	2214	$20\frac{1}{2}$ , 2211.97
	$\sigma_4$	68.64	1294	12, 1310.8	1304	12, 1310.8
	$\sigma_1 \dots \sigma_4$	584.79	10924.8	100, 10923.3 $\pm$ 2	11007.9	$100\frac{1}{2}$ , 11005.2 $\pm$ 2
			+19d $\nu$ - 383 $\xi$			

In  $\phi_1, \sigma_4$  is mean of 1.62, 1.52, of which the latter is the more reliable. It would make the final  $\Delta$  1385.7, 1420.6.

\* Back, *Z. f. Phys.* xv. p. 206 (1923).

The  $-\xi$  would increase the former, the latter is exact 138 within errors.

In  $\phi_2$  the small coefficient of  $d\nu$  makes the conditions more exigent. The S' hypothesis here also best satisfies our old conditions, especially when the S" data are modified by the  $-\xi$  condition. There are therefore good grounds for suspecting that the S' hypothesis is correct and that the new sequences obey the old rules subject to some multiplet modification analogous to the old "triplet."

#### IV. Displacement in the Manganese Spectrum.

We come now to the consideration and discussion of the statement made above that the normal representatives of the S and D triplets for orders of  $m=6$  and beyond are disrupted into congeries of displaced lines. For the sake of readers not familiar with this condition it may be convenient to begin with some remarks on displacement in general. When a change takes place in the mantissa of the function  $N/(m + \text{mantissa})^2$  which gives the value of a term, the new line is said to be displaced and its wave number is shifted a definite amount. *E. g.*, in Mn,  $p_1$  is  $N/(1.630526)^2$ . If we deduct a quantity .003420 from the mantissa,  $N/(1.627106)^2$  gives  $p_2$  and  $p_2$  is shifted from  $p_1$  by  $\nu_1 = 173.62$ . Here the displacement 3420\* is  $31\frac{1}{2}\delta$  or 125 oons. A further displacement of 2532, or 93 oons, shifts to  $p_3$  by  $\nu_2 = 129.24$ . In general—and always in the recognized series—the wave number of a line depends on the difference of two terms, and displacement may occur in each term, giving a line shifted from the original. This for example occurs in diffuse series where the doublet or triplet separations are produced by displacements in the limit  $p_1$ , and the satellites by displacements in the  $d(m)$  term. In practically all known cases the displacement value is a multiple of the oon. A line displaced from a given one is represented by writing the displacement on the limit (or first term) before the line symbol and that on the sequence or second term after. Thus  $D_{22}(m)$  is  $(-x\delta) D_{11}(m)(-y\delta)$ , where  $x\delta$  is deducted in  $p_1 - 31\frac{1}{2}\delta$  in the above example—and  $y\delta$  is deducted in the  $d_1$ . For example, in Mn the line 3547.792 or  $D_{22}(2)$  is  $(-21\frac{1}{2}\delta) D_1(2)(-2\frac{1}{2}\delta)$ .

Now it is found that this shifting or production of new lines by displacement is a very common effect and not confined to the multiplets of the generally recognized series.

\* It is convenient to treat the mantissa as multiplied by  $10^6$ .



It is especially common in connexion with the higher order of series lines, the actual series lines being either reduced in intensity or absent and replaced by several displaced representatives or "collaterals." The effect may take place when the excitation is produced by the arc, but even more copiously when the spark is employed. It is a common fetish to regard a spectrum produced by a spark as depending wholly on ionized elements with the exception of a few stubborn series lines of the neutral element which have managed to survive. Collaterals are also found in rich arc spectra, but linkages seem to be a special feature of those of the spark. Indeed in the present case the arc spectrum of Mn, as observed by Fritsch, terminates just beyond the Sand D limit—*i.e.* extreme limit of displacement—whilst the spark by Exner and Haschek continues very considerably beyond—*i.e.* to link possibilities. It is probable that when a spectrum by the spark is rich in lines, the richness is due largely to the prevalence (1) of collaterals of neutral atomic series lines, and (2) of linkages to individual series lines. Such collaterals are to be looked for in the neighbourhood of the higher series lines, and their existence often enables us to reconstruct the normal series representative, even when it has itself disappeared. They often indicate themselves by showing repeated separations close to those of the normal doublets or triplets. Frequently, also, we find a number of lines close together, separated from one another by amounts which are multiples of some common factor. In such a case they may be suspected to be collaterally related, and if this common factor corresponds to the shift produced by an own displacement in one of the terms of the series line in question, it is good evidence that they are actually collaterals. It must of course not be forgotten that a single numerical agreement may be a chance coincidence, and must not be regarded as a proof by itself of actual collateral relation.

As in general displacement may occur in two terms, the identification of a single line as such a collateral of another is not easy\*. But for our present purpose we are dealing with high order lines, and in this case the shift per own in the sequence term is exceedingly small, and a small fraction of the observation errors. Consequently any observed shift is almost wholly due to displacement in the limit term alone. If large displacements on the sequence term also occur, the above regularities will not appear, and the collateral would not thus be recognized.

\* For some examples see 'Analysis,' p. 139.

We proceed to illustrate the above remarks by a discussion of the observed data in regions corresponding to S (6, 7) and D (5, 6, 7). In doing so, the object is not so much to determine the value of series lines themselves as to give evidence for the displacement effect and to illustrate method. Consequently we shall have to adduce a considerable quantity of data which the application of the method may show to be irrelevant.

For any number of ouns here dealt with, the shift in any case will be very nearly proportional to the number taking part in a displacement. The shifts per oun displacement are 1.3816 in  $p_1$ , 1.3911 in  $p_2$ , and 1.3968 in  $p_3$ . Those for  $s_6$ ,  $d_5$ ,  $d_6$ , are respectively .023, .029, .018. For the sake of reference the shift multiples up to 12 and for 16, 20, 24 are here given :—

	1.	2.	3.	4.	5.	6.	7.	8.
$p_1$ .....	1.38	2.76	4.14	5.53	6.91	8.29	9.67	11.05
$p_2$ .....	1.39	2.78	4.17	5.56	6.95	8.35	9.74	11.13
$p_3$ .....	1.40	2.79	4.19	5.59	6.98	8.38	9.78	11.17
	9.	10.	11.	12.	16.	20.	24.	
$p_1$ .....	12.43	13.82	15.20	16.58	22.10	27.63	33.16	
$p_2$ .....	12.52	13.91	15.30	16.69	22.26	27.82	33.39	
$p_3$ .....	12.57	13.97	15.36	16.76	22.35	27.94	33.52	

Deviation from proportionality for  $x$  ouns =  $\pm 0.0000350 \cdot x$  for  $\mp x$ , or shift per oun on  $(x\delta_1)p = 0.0000350 (2x + 1)$ .

As the formula gives the exact value for S (5) we may feel confidence in its reliability for higher orders. For S (6, 7) it gives wave numbers 38547.05 and 39233.45. In the following, Fritsch's measures in the arc and those of Exner and Haschek's in the spark are used with wave numbers expressed in  $1/\text{\AA}$ . All successive observed lines are taken in each region. The first wave-lengths in each are 2595.847, 2584.432, 2576.284. Separations of successive lines are shown with deviations from oun shifts, the shift per oun being denoted by  $s$ . Those accepted as obeying the multiple law are indicated by an asterisk.

In the  $S_1$  set 38541 definitely has no multiple shifts, and indeed the line cannot belong to the S system since it is strongly enhanced in the spark. Of the others we get displacement evidence as between (1, 2, 5) in the arc and (2, 3) in the spark respectively with  $18s + .03$ ,  $12s - .05$ ,  $10s - .03$ . It should be possible to determine a very accurate estimate of the normal line taking the calculated value as a guide.

	No. I.	Arc.	I.	Spark.
$S_1$	1 5, 38512.85	24.90 $18s + .03*$	2, 38497.25	16.90 $12s + .32$
	2 2, 37.75	3.92 $3s - .22$	3, 514.15	13.79 $10s - .03*$
	3 4, 41.67	3.13 $2s + .37$	2, 527.94	
	4 4, 44.80	9.48 $7s - .19$		
	5 5, 54.28			
	(5)-(2)=16.53 $12s - .05*$			
$S_2$	1 4, 38682.95	2.88 $2s + .10*$	2, 38703.34	5.40 $4s - .16$
	2 4, 85.83	12.35 $9s - .17$	1, 08.74	2.85 $2s + .07*$
	3 3, 98.18	.69	1, 11.59	11.09 $8s + .04*$
	4 3, 98.87	1.98	1, 22.68	
	5 2, 700.85	.88		
	6 1, 01.73	19.73 $14s + .28$		
	7 1, 21.48			
	(3)-(1)=11.8-.07*; (5)-(3)=2s-.11*; (6)-(4)=2s+.08*.			
$S_3$	1 5, 38805.23	9.87 $7s + .09*$	4 R, 38806.53	9.04
	2 5, 15.15	6.53	2, 15.57	19.00
	3 1, 21.68	3.72	1, 34.57	22.03
	4 1, 25.40	6.23	1, 56.60	5.14
	5 1, 31.63	.77	1, 61.74	8.15
	6 1, 32.40	23.70 $17s - .05*$	1, 69.89	14.51
	7 5, 56.10		2, 84.40	
	(5)-(2)=12s-.28; (6)-(4)=5s+.01*.			
	(6)-(2)=39s-.10*; (7)-(4)=29s-.12.			

Treating the arc lines as displaced 25, 7, -5 ouns on  $S_1$ , *i. e.* shifted 34.54, 9.67, 6.91 and the spark as displaced 24, 14 ouns or shifted 33.16, 19.34, we find

arc ...  $S_1(6)=38547.39, .42, .37$ , mean  $38547.393 \pm .023$   
 spark... ,, = ... 47.31, .28, ,,  $38547.295 \pm .015$ .

The difference between the two means is not larger than that to be expected between the absolute measures of two observers, here Fritsch and Exner and Haschek. The arc mean gives  $O-C \, d\lambda = -.02$ .

In  $S_2$  we take (1, 2, 3, 5, 7) in the arc as displaced by 27, 25, 16, 14, -1 ouns giving shifts 37.53, 34.76, 22.26, 19.47

—1.39 and (1, 2, 3, 4) in the spark by 12, 8, 6, —2 ouns with shifts 16.69, 11.13, 8.35, —2.78. The results are

are ... 38720.48, .59, .44, .32, .09, mean 38720.384  
spark ... 20.03, 19.87, .94, .90, ,, 38719.935.

But although these are strikingly mutual limit collaterals they do not give a value of  $S_2$  corresponding to  $S_1(6)$ . The other set (4, 6), however, do. Regarded as 16, 14 oun displacements or shifted 22.26, 19.47 they give for  $S_2(6)$

38721.13, .20, mean 38721.16;  $\nu_1=173.77$ .

The first set correspond to a .8 shift on the  $s(6)$  term, about a 35  $\delta_1$  displacement.

In  $S_3$ , (1) in the arc is a greatly enhanced line in the spark (4 R to 30 R) and the agreement in (2)—(1) is probably a chance coincidence. (4, 6, 7), as displaced 18, 13, —4 ouns or shifted 25.14, 18.14, —5.59 give 38850.54, .54, .51, mean 38850.53, with  $\nu_2=129.37$ , in good agreement. The spark measures definitely exclude the enhanced line, and it is remarkable that out of the 15 possible combinations of the other six spark lines only two sets show a multiple connexion accepted only because the observation errors in the spark are larger. The arc lines (2, 5) with 25, 13 ouns and shifts 34.90, 18.16 and the spark (2, 6) with 25, —14 ouns and shifts 34.90, —19.56 give

are ... 38850.05, 49.79, mean 38849.92  
spark ... 50.47, .33, ,, 38850.40.

The spark may correspond to the former arc set. The arc set here give  $\nu_2=128.76$ , and they correspond therefore to lines also displaced about 24 ouns in  $s(6)$  (shift = .51).

The final results for the  $S(6)$  triplets are thus :

38547.39  
173.77  
38721.16  
129.37  
38850.53

The fact that with so large a factor as 1.4 we get such close agreement in so many cases is very striking.

In further support of the displacement effect we may notice the following sets with triplet separations.

A.	B.	C.	D.	E.
35512.85	38554.28	38527.94 <sub>s</sub>		38537.75
<b>172.98</b>	<b>173.66</b>	<b>172.91</b>		<b>173.84</b>
635.83	727.94	700.85	38701.73	711.59 <sub>s</sub>
<b>129.32</b>	<b>128.68</b>	<b>130.78</b>	<b>130.67</b>	<b>172.81</b>
815.15	856.62	831.63	832.40	884.40 <sub>s</sub>

These illustrate the fact that where doublets or triplets are disrupted into collaterals we find a considerable number of sets in the neighbourhood with separations nearly, but not the same as the normal ones. Here

A is Catalan's suggestion for  $S(6)$ . It is the set  $(25 \delta_1) S(6)$  with  $O-C \, d\lambda = -.02$ . The displacement of 25 ouns requires a diminution of  $\nu_1 + \nu_2$  by  $.38$  to  $302.48$ . The observed  $302.30$  is within observation errors of this.

B is  $(-6\delta_1) S(6)$ :  $O-C \, d\lambda$  on  $S_1=0$ .

C. The first two form the set suggested in the 'Analysis.' They are  $(7\delta_1) S_{1,2}(6)$ .

The calculated values for  $D(5, 6, 7)$  are  $38097.29, 38947.73, 39495.44$ . In the region of  $D_1$  there are few spark lines, and these represented in the arc. There is a gap in the arc lines after  $38300$ , whilst the spark is rich. Consequently for  $m=5$  we take arc lines for  $D_1$  and spark for  $D_3$ . The calculated  $D_1$  is directly observed at  $38097.37$ . The separations from this—or corresponding  $D_2, D_3$ —are entered in the list with the multiple deviations. The first wave-lengths in each region are  $2625.226, 2613.669, 2604.44$ .

$D_1(5)$ arc.			$D_2(5)$ arc.			
1	2,	38081.88	11 s + .29	2,	38250.27	15 s - .14 *
2	4,	86.52	8 s - .20	4,	60.95	7 s + .30
3	1,	88.20	7 s - .50	1,	65.03	4 s + .40
4	4,	97.37	0 *	4,	300.23	-21 s - .03 *
5	4,	108.41	- 8 s + .01 *	(3)-(2) = 4.08 = 3 s - .09 *		
6	5,	14.02	-12 s - .07 *	(5)-(1) = 49.96 = 36 s - .08 *		
7	1,	37.45	-29 s - .01 *			
$D_2(5)$ spark.			$D_3(5)$ spark.			
1	1,	38243.52	20 s - .35	2,	38385.80	10 s + .46
2	1,	64.15	5 s - .11 *		87.91 †	9 s - .25
3	1,	90.08	-14 s + .38	3,	95.09	4 s - .44
4	1,	94.04	-17 s + .60	1,	402.60	-2 s + .42
5	1,	300.20	-21 s + 0 *	1,	03.80 §	-3 s - .62
6	2,	09.30	-28 s + .64	1,	04.52	-3 s - .10 *
7				3,	09.68	-7 s + .33
8				1,	18.39	-13 s + .0 *
(6)-(4) = 15.26 = 11 s - .04 *.			(7)-(4) = 7.08 = 5 s + .10 *.			

† Corrected from Catalan's ...89.4. § Arc.

In  $D_1(4, 5, 6, 7)$  give  $D_1 5 = \text{mean of } 38097.37, .36, .44, .37 = 38097.387$ . For  $D_2, 38300$  arc and spark is enhanced and

had best be excluded. In the arc (3, 2) require also displ. in  $d(5)$  (of about .35), as also 6, 4 in the spark (of about .6). (2) in spark is good. It gives  $D_2 5 = 38271.10$ .  $D_3 5$  from (6, 8) is mean of  $38400.33, .23 = 38400.280$ .

The D (5) set is thus

38097.387		O-C $d\lambda = -.007$
	<b>173.71</b>	
38271.10		<b>302.89</b>
	<b>129.18</b>	
38400.280		

Here the  $\nu_1, \nu_2$  are practically exact normal separations. Amongst the above are

(8 $\delta_1$ ) D, 38086.52	(-12 $\delta_1$ ) D, 38114.02	38265.03
	<b>174.43</b>	<b>129.50</b> <b>130.06</b>
260.95	<b>301.39</b>	243.52 395.09
	<b>126.96</b>	
387.91		

The first set is Catalan's allocation for D(5), but the separations are abnormal. For a set (8 $\delta_1$ )D the triplet separations should be 173.54, 129.20, sum 302.74. The deviations are greater than can be accounted for by observation errors and must be due to displacements in  $d(5)$ .

The lines for S(7), D(6, 7) and beyond become intermixed. The number of spark lines is so large that we will omit their consideration except where absence of collaterals appear amongst those of the arc. Take the arc lines from 2567.529 to 2527.539.

D <sub>1</sub> 6	1	1,	38937.60	10.13		13	2,	39255.83
						14	1,	312.75
	2	2,	55.51	- 7.78		15	3,	14.45
	3	3,	58.67	-10.94, - 8 s + .11		16	3,	18.88
	4	2,	59.51	-11.78		17	4,	25.24
	5	2,	70.86	-23.13, -17 s + .36		18	1,	62.12
	6	3,	94.66†			19	3,	63.91
	7	2,	39001.32	-53.59, -39 s + .35		20	3,	67.88
	8	2,	59.31	62.04, 45 s - .49	S <sub>1</sub> 7			
	9	3,	98.52	22.88		21	4,	465.79
D <sub>2</sub> 6	10	1,	102.32	19.02, 14 s - .44	D <sub>1</sub> 7			
						22	1,	68.67
	11	1,	40.89	-19.54, -14 s - .07		23	4,	502.71
	12	4,	222.52		S <sub>1</sub> 7			
S <sub>1</sub> 7, D <sub>3</sub> 6						24	5,	53.62

† Enhanced line.

Taking first (1 ... 7), as in the region of D<sub>1</sub>(6), the numbers entered on the right are separations from the calculated

$D_1(6)$ . (3) as  $(-2\delta)D_1(6)$  gives  $D_1(6)=38947\cdot62$ ,  $O-C$   $d\lambda=.007$ . (5, 7)—separation  $=22s+.01*$  have the same  $d$  sequence but probably displaced from the normal  $d(6)$ . Also (1, 2, 4?) separated by  $17\cdot91$ ,  $4\cdot00$ , or  $4s-.05*$ ,  $3s-.14(?)$  are possible mutual limit collaterals, displaced also by the same amount in their  $d$  terms.

(8...11) are in the  $D_2(6)$  region. Of these (8, 10) are relatively shifted by  $31s-.05*$ . (11) as  $(-14\delta_1)D_2(6)$  gives  $D_2(6)=39140\cdot89-19\cdot47=39121\cdot42$ . It and (10) will be equally and oppositely displaced  $\pm 14\delta_1$  in the limit, and (10) in addition by a small one in  $d$ .

The four or more lines beyond (12) are in the neighbourhood of  $S_1(7)$  and  $D_3(6)$ . These both lie between (12) and (13). These are separated by  $33\cdot31$  which is  $24s+.15$  if both are related to  $S_1$  and  $24s-.20$  if to  $D_3$ . They cannot therefore be mutual limit collaterals. The smallest displacements would suggest allocating (12) to  $S_1$  and (13) to  $D_3$ , but this is no necessary condition, and indeed if (12) be a  $D_3$  line it gives a correct  $\nu_1+\nu_2$  with the  $D_1$  determined above. Thus (12) as displaced  $20\delta_1$  gives  $D_3(6)=39222\cdot52+27\cdot92=39250\cdot44$  and the whole set give  $\nu_1=173\cdot80$ ,  $\nu_2=129\cdot02$ ,  $\nu_1+\nu_2=302\cdot82$ .

In this case (13) cannot be a limit displacement of  $D_3$ , but if it is connected with  $S_1(7)$  it is displaced  $-16\delta_1$  and gives  $S_1(7)=39255\cdot83-22\cdot11=39233\cdot72$  with  $O-C$   $d\lambda=-.02$ . But there is little supporting evidence for the allocation.

$S_2(7)$  comes between (20, 21) and  $D_1(7)$  between (21, 22). The separations of (20, 21) from the calculated  $S_2$  are  $39\cdot19=28s+.27$  and  $-58\cdot72=-42s-.22$ . Their mutual separation is thus  $70s+.49$  so that they cannot be mutual limit collaterals. (20) as  $(28\delta_1)S_2$  gives  $S_2(7)=39367\cdot88+38\cdot92=39406\cdot80$ ,  $O-C$   $d\lambda=-.017$ .  $S_3(7)$  comes between (23, 24), separated by  $50\cdot91=36s+.62$ , and consequently not mutual limit collaterals. (23) as  $(24\delta_1)S_3$  gives  $S_3(7)=39502\cdot71+33\cdot50=39536\cdot21$ ,  $O-C$   $d\lambda=.006$ . The absence of collaterals in the arc lines for the  $S(7)$  set, however, renders the evidence precarious as it depends only on a general agreement with formulæ values. In its favour is the fact that the resulting  $\nu_2$  separation  $129\cdot41=\nu_2+.17$  is good, although the  $\nu_1$ ,  $172\cdot08=\nu_1-.54$ , is bad. There are few arc lines in the neighbourhood although the spark are numerous, but not so well measured. *E.g.* the spark lines  $\lambda\lambda 2537\cdot45$ ,  $2536\cdot91$  or  $nn.39399\cdot13$ ,  $39407\cdot52$ , separated by  $8\cdot39=6s+.05$  for  $S_1$ , are mutual limit collaterals, and, as  $(6\delta_1)S_2$  and  $S_2$  give  $39399\cdot13+8\cdot35=39407\cdot48$  and  $...07\cdot52$ , mean  $39407\cdot50$ , close to the calculated  $...07\cdot07$ . We should not

expect the normal  $S_2$  to appear in the spark and not in the arc. This is therefore probably not the true  $S_2(7)$ , but the two are displaced by the same amount in the  $s(7)$  term.

(21, 22) are separated by  $2.88 = 2s - .12$  and may possibly be mutual limit collaterals. Regarded as displaced by  $22\delta_1$  and  $20\delta_1$  they give for  $D_1(7)$   $39465.79 + 30.40 = \dots 96.19$  and  $\dots 68.67 + 27.64 = \dots 96.31$ , mean  $D_1(7) = 39496.25$   $O - C \, d\lambda = -.05$ .

There are no arc lines in the  $D_{2,3}(7)$  regions. The series lines here require the spark for collaterals, and these give evidence for displacement. *E.g.*, for these regions, beginning at  $\lambda = 2521.77$  and  $\lambda = 2514.75$ , we find

	$D_{2,3}$		$D_{2,3}$
1	1, 39644.10	1.	39754.76
2	1, 52.28	2,	61.72
3	2, 61.40	2,	817.29
4	1, 66.28	1,	34.10
5	1, 68.49		
6	2, 99.16		

In the first column two different sets satisfy the conditions of mutual displacement, viz. (1, 2, 4) with separations  $6s - .17$ ?  $10s - .09$ , and (3, 5, 6) with  $5s + .13$ ,  $22s + .05$ . (5) is very near to  $D_27$ , but we should not expect the spark to produce a series line when the arc does not; so that it probably belongs to another series line. Indeed they satisfy  $S_1(8)$  which is given by the formula as 39688.16. Taking (1, 2, 4) as 18, 12, 2 ouns on  $D_27$  and 6 as  $-8$  on  $S_1(8)$  gives

$$D_27 = 39669.14, 8.97, 9.06, \text{ mean } 69.056, O - C \, d\lambda = -.001, \\ S_18 = 39699.19 - 11.05 = \dots 88.14.$$

In the right-hand column there are again two sets of mutual collaterals (1, 2) and (3, 4) with  $5s - .02$ , and  $12s + .05$  on the  $p_31$ . The first two as 31 and 26 ouns on  $D_3$  give for  $D_3(7)$

$$39798.04, 02, \text{ mean } 39798.03, O - C \, d\lambda = .015.$$

The foregoing discussion gives evidence of the existence of displaced series lines as a general phenomenon. The actual suggestions for individual series lines in  $S(m)$ ,  $D(m)$ , cannot be proved to be correct owing to the existence of displacement on the current  $s(m)$ ,  $d(m)$  sequences, but it is noticeable how closely they reproduce the independent series separations  $v_1, v_2$  and how closely they conform to values calculated from the formulæ, of which the  $S$  formula has been shown to reproduce one undoubted set with exactness.



The results of the discussion are here collected :—

	6.	7.	8.
S	{ 38547.39	39233.72	39688.14
	173.77	173.08	
	{ 38721.16	39406.80	
	129.37	129.41	
	{ 38850.53	39536.21	
D	5.	6.	7.
	{ 38097.39	38947.62	39496.25 ?
	173.71	173.80	172.81
	{ 38271.10	39121.42	39669.06
	129.18	129.02	128.97
	{ 38400.28	39250.44	39798.03

The wave-lengths of the various lines involved are appended. The figures in brackets denote the number of lines the limit must be displaced to produce the series line. Thus  $(-25)2595 = S_1(6)$  or 2595 is  $(25\delta_1) S_1(6)$ . The numbers on the left of a line give the intensity. The measures are in R.A.

$S_1(6)$ . Arc 5,  $(-25)2595.847$ ; 2,  $(-7)...4.170$ ; 5,  $(5)3.057$ .

Spk. 3,  $(-24)...95.76$ ; 2,  $(-14)...4.83$ .

$S_2(6)$ . „ 3,  $(-24)2583.369$ ; 1,  $(-14)...3.178$ .

Spk. 2,  $(-12)...3.07$ ; 1,  $(-8)...2.71$ ; 1,  $(-6)...2.52$ ; 1,  $(2)...1.78$ .

$S_3(6)$ . „ 5,  $(-25)2575.629$ ; 1,  $(-13)...4.536$ .

Spk. 1,  $(-25)...5.60$ ; 1,  $(14)...2.00$ .

$S_1(7)$ . 2,  $(16)2546.713$ .  $S_2(7)$ . 3,  $(-28)...39.465$ .  $S_3(7)$ . 4,  $(-24)...30.797$ .

$S_1(8)$ . 2,  $(8)2518.27$ .

$D_1(5)$ . 4,  $2624.158$ ; 4,  $(8)...3.368$ ; 5,  $(12)...3.011$ ; 1,  $(29)...21.40 s$ .

$D_2(5)$ . 1,  $(-5)2612.72$ ; 1,  $(-20)...4.13$ ; 1,  $(14)...0.95$ .

$D_3(5)$ . 1,  $(3)2603.17$ ; 1,  $(13)...2.23$ .

$D_1(6)$ . 3,  $(2)2566.140$ .  $D_2(6)$ . 1,  $(14)...54.193$ .  $D_3(6)$ . 4,  $(-20)...48.877$ .

$D_1(7)$ . 4,  $(-22)2533.165$ ; 1,  $(-20)...2.980$ .

$D_2(7)$ . 1,  $(-18)2521.77$ ; 1,  $(-12)...1.25$ ; 1,  $(-2)...0.36$ .

$D_3(7)$ . 1,  $(-31)2514.75$ ; 2,  $(-26)...4.31$ .

$S_2(6)(-30\delta_1 \pm)$ . 4,  $(-27)2584.432$ ; 4,  $(-25)...4.240$ ; 3,  $(-16)...3.415$ ;

2,  $(-14)...3.237$ ; 1,  $(1)...1.860$ . Arc.

We now turn to the consideration of the nature of the two parallel narrow triplets. We will denote their formulæ by  $p - \phi m$ ,  $d - \phi n$ , the question being whether the  $p$  is a singlet limit and thus determined indirectly without reference to the series itself, or whether the series is to be regarded as independent and  $p$  directly determined from it. We are to test this by examining which of the formulæ is the better supported by the observed data. The series lines themselves will be denoted by  $S'$ ,  $D'$  or  $S^n$ ,  $D^n$ , the dash referring to singlet and  $n$  to narrow series and  $D$  to the limit  $d$ . The two formulæ give for  $m=4$

$$S^n = 18868.53,$$

$$S' = 18784.95,$$

$$D^n = 29836.28,$$

$$D' = 29752.70.$$

The separations are  $\nu_1 = 44.11$ ,  $\nu_2 = 35.87$ ,  $\sigma_1 = 14.22$ ,  $\sigma_2 = 8.70$ . The wave-numbers of the lines observed in these neighbourhoods are given in the two lists below, beginning with  $\lambda = 5331.479$  and  $\lambda = 3366.361$  respectively.

List S.				List D.					
1	1,	18751.61	33.80	( $\Delta_1 + 2\Delta_2$ )X <sub>1</sub>	1,	29698.14	44.54	(10 $\delta_1$ )D <sub>1</sub> '	1
2		85.41+		S <sub>1</sub> '	3,	742.68	50.67	$a.(-3\delta_1)D_1''$	2
3	1n,	18813.34	27.43	$45s = 29.16, 7.02*$	1,	63.35	7.53	$b.(-10\delta_1)D_1''$	3
4	1n,	15.07	1.73		2,	800.88	26.13		4
5	1n,	20.46	5.39	$9s = 5.64, .60$	2,	27.01	2.34		5
6	1n,	22.22	1.76	$3s = 1.88, .86$	1,	29.55+	9.09	(- $\delta$ )D <sub>1</sub> ''	6
7	3n,	31.07	8.85	$14s = 8.78*, .71$	2,	38.44	9.02		7
8	3n,	66.95	35.88		3,	47.45	35.17		8
9	2n,	70.10	3.15	$5s = 3.143*, .117$	2,	83.63	14.54	(-5 $\delta_1$ )D <sub>1</sub> ''	9
10	1,	87.88	17.78	$38s = 17.62, .46$	3,	98.17		(-5 $\delta_1$ )D <sub>2</sub> ''	10
11	2n,	18900.40	12.52	$20s = 12.61*, .56*$					
12	1,	02.35	1.35	$3s = 1.89*, .87*$					
13	1,	37.75	35.40	(- $\Delta_2 + 2\delta_1$ )S <sub>3</sub> '					
14	1,	54.94	17.19	(- $\Delta_2 + 2\delta_1$ )S <sub>3</sub> '					
				(- $\Delta_2 + 2\delta_1$ )S <sub>3</sub> '					
				$b.(\delta_1)X_3$					
				(- $\Delta_2 - \delta_1$ )S <sub>3</sub> '					
				$b.(\delta_1)X_3$					
				(-2 $\Delta_2$ )S <sub>3</sub> '					
				$b.(-\Delta_2 + 2\delta_1)X_3$					
									</

These are all the lines observed by Fritsch in the  $S(4)$ ,  $D(4)$  regions together with (6) in list D by Exner and Haschek and (2) in List S. The latter is taken from Kayser's *Handbuch* as observed by Rowland in the sun. It has not been observed in the arc or spark by Hasselberg, Fritsch, Kilby, Fuchs, or King. It practically corresponds to the calculated  $S'(4)$  and is the only line in the neighbourhood. The question of its reality is therefore crucial as regards the singlet hypothesis. There is no corresponding line for  $D'(4)$ . The calculated  $S^n(4)$  comes half-way between (8, 9), whilst in list, D, (7) is 10967 ahead and is  $D^n(4)$ .

The first thing to be noticed is the large number of separations close to those of the S triplets. They are shown in the subjoined diagrams, which recall at once the meshes and chains of a linkage system. The figures in thick type refer to the numbered lines in the list. This repetition is a

	1	79.47	7						
	33.80		45.66	35.88					
S.		2	35.05	46.49	8	35.40	12	35.40	13
			36.81	5	44.73				
				6					
					8				
				46.58	36.17				
D.			4	37.56	45.19	9	14.54	10	
					7				
				45.09					
	1	44.54	2	50.67	3	36.00	6		

striking characteristic in many spectra and is a certain sign of multiple displacement, or linkage. Here, in the second list where displacement can only occur in  $d$  or  $\phi_1$ , the appearance of  $p$  separations cannot be due to displacement, and their presence here points to the linkage effect. In the first list their appearance may be due either to links, or displacement, or both.

We will now examine in more detail the data in the first list. The shifts per  $\delta$  ( $=4\delta_1$ ) will be slightly different on the two hypotheses, viz. 2.5150 for  $p^n$  and 2.4818 for  $p'$ —the first near  $S_1^n$  at (8) and the second near  $S_1'$  at (2). The changes in these after a displacement of  $x\delta$  are practically the same, viz. .000194( $2x+1$ ). The shifts per  $\phi$  are printed on the left of the wave-number, those due to  $p'$  being in italics, on the supposition that no linkages enter. The shifts per  $\phi$  in  $d_1$  are 1.0971 and 1.0871. The shift per  $\phi$  in  $\phi^n(4)$  is .0679 and in  $\phi'(4)$  is .0655. The successive

separations are given in the column next the wave-number and are followed by the nearest own shifts on the two hypotheses. It will be seen that the independent hypothesis gives the best agreement. The separation 1·7, which appears twice, cannot be due to limit shifts alone. If due to displacement in  $\phi$  alone, 26 ouns shift 1·76 or 1·70.

First consider the data on the basis of  $S^n$ . The calculated value comes just half-way between (8) and (9), which are definitely mutual limit collaterals of five ouns. The line (9) is separated from (7) in the second list by  $10967\cdot75 + \cdot59$ . As  $\cdot59$  is within error limits of  $\cdot62$  it is natural to take the (7) as the representative of  $D^n(4)$  and the (9) as too small by  $\cdot62$ ; in other words it represents  $(\delta_1)S_1^n(4)$ . But as (8) is the stronger line with numerous links, it will be better to take it as our starting point and denote it by  $X_1$ , with a limit near  $p_1^n$ . Then (9) is  $(-5\delta_1)X_1$ . (6) is  $44\cdot73$  behind (8). If this is a linkage, the link is  $b + \cdot62$  ( $b = \nu_1$ ) and the line  $b \cdot (\delta_1)X_1$ . Now a  $(-b)$  link would bring  $X_1$  back  $\nu_1$ ,  $X_2$  to coincide with  $X_1$  and  $X_3$  to a line  $\nu_2 = 35\cdot87$  ahead of  $X_1$ . We find a line (12)  $35\cdot40 = \nu_2 - \cdot47$  ahead, but  $\cdot47$  is no oun shift. But if  $X_3$  be linked back by the  $a$  link instead of the  $b$ , it should be  $35\cdot99$  ahead  $= 35\cdot40 + \cdot59$ , the  $\cdot59$  being within reach of an oun shift. But this seems artificial, and it is more probable that displacement occurs in  $\phi$ . Consequently (12) is entered as  $b(\delta_1)X_3$ ,  $X_3$  being regarded as suffering a small displacement in  $\phi$  of two or three ouns. Thus (6.8.12) give a triplet linked back by  $b$  from (8). Although this bodily shift of the triplet is exact we do not expect to find, especially in an arc-excited spectrum, that the normal lines wholly disappear when linked. But we have just seen that (8) may be both  $S_1$  and  $b \cdot S_2$ , since the two are necessarily the same. In this case the normal  $S_2, S_3$  have disappeared. There is a great deal to be said therefore for this allocation. (7) is an exact  $\nu_2$  behind (8) and it would appear as the linked line  $\nu_2 \cdot X_1$ , but we have no evidence in other spectra of  $\nu_2$  acting as a link. If it is  $(\Delta_2)X_1$ , the separation would be  $35\cdot56$  and not permissible without concurrent displacement in  $\phi(4)$ . But (8) is, as shown above, also  $b \cdot X_2$  and  $(\Delta_2)X_2$  produces a shift close to the observed  $35\cdot88$ , or (7) is  $b \cdot (\Delta_2)X_2$ , and is entered thus.

(13) is  $35\cdot40$  ahead of (12). A displacement  $-\Delta_2$  on  $X_3$  in (12) shifts  $35\cdot97$ , or  $35\cdot40 + \cdot57$ , i.e. an additional  $\delta_1$ . The line is  $b \cdot (-\Delta_2 + 2\delta_1)X_3$ .

(13, 14) are not mutual collaterals and (14) remains undetermined.

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(10, 11) are mutual collaterals with (12) and are therefore  $b.(\delta)X_3$  and  $b(6\delta)X_3$ .

(1) is 79.46 behind (7). If linked by  $\nu_1 + \nu_2$  it is .42 in defect; if displaced  $\Delta_1 + \Delta_2$ , the shift is 79.64 or .18 in defect. It is numerically  $(\Delta_1 + 2\Delta_2)X_1$ , as if (7) were  $(\Delta_2)X_1$ .

The uncertain line (2) by Rowland is 79.52 behind (8). A displacement of  $\Delta_1 + \Delta_2$  on  $p_1$  gives 79.64, the same within error limits of the two different observers.

(3) is a 14 oun shift on (6). It is  $b. (15\delta_1)X_1$ .

Even if not correct in all details, the foregoing discussion affords strong evidence of a linked and displaced congeries of lines based on the line (8), which we have denoted by  $X_1$ .

What is the relation of  $X_1$  to  $S_1$ ? The system is clearly built on  $X_1$ . We have the triplet set  $b.(\delta_1)X_1$ ,  $X_1$  or  $b.X_2$ , and  $b.(\delta_1)X_3$ , or say if  $X_1 = (-\delta_1)S_1^n$  the set  $b.S_1$ ,  $b.(-\delta_1)S_2$ ,  $b.S_3$ . Now the line 29838.44, which is 10968.34 = 10967.75 + .59 from (9) would seem to point to (9) with a  $\delta_1$  displacement as the true  $S_1$ . But there may be displacement on the line 29838 as well. If  $X_1$  is true  $S_1$  the true  $D_1$  is 29834.68; whereas if  $X_1 = (-\delta_1)S_1$  the true  $S_1$  is 18166.30 and the true  $D_1 = 29834.05$ . These are respectively 3.76 and 4.39 behind the observed line. The shift per oun is here 1.0971, of which 3.76 is no multiple, whilst a 4 oun or  $\delta$  shift is 4.388 or exact. Thus the combined evidence points to 18166.30 as the true  $S_1^n(4)$  and 29838.44 is  $(-\delta)D_1^n(4)$ . This gives the O-C error of the calculated  $S_1$  as  $dn = -2.23$  or  $d\lambda = .62$ . This can be explained by the limit having been taken too large by a few units—easily the case, since it was determined by using the first three lines of the series. We should then expect to find that the calculated  $S_{1.5}$  should be in excess by a quantity greater than 2. Indeed, if the formula be calculated from  $m=2, 3$  and this for  $m=4$ , the limit is 5.75 less and the calculated for  $m=5$  is 20719.19.

When we now proceed to test the data on the supposition that (2) is near the true  $S_1'$  we have the uncertainty as to the relative separations due to the fact that (2) is due to a different observer. *E.g.*, if it is correct, (3) is an exact limit collateral, but in the triplet (2.7.8) whilst  $\nu_2$  is correct the  $\nu_1 = 45.66$  is 1.55 in excess and cannot be a pure displacement ( $1.55 = 2$  oun shifts + .32). Since we have here an otherwise good triplet we shall take the .32 as an obs. error, in which case (3) must be taken as not a limit displacement of (2), and 7, 8 become  $(-2\delta_1)S_2'$ ,  $(-2\delta_1)S_3'$ .

(12) is 35.40 ahead of (8). An additional  $\Delta_2$  displacement shifts 35.96 or .56 too large, .61 being equivalent to an additional  $\delta_1$ . Thus (12) is  $(-\Delta_2 - \delta_1)S_3$ . (10, 11) are related to 12, as in the former case.

(13) is 35.40 ahead of (12), *i. e.* of  $(-\Delta_2 - \delta_1)S'_3$ . An extra  $\Delta_2$  displacement shifts 36.03, requiring .63 less or  $+\delta_1$  on the limit. It is therefore  $(-2\Delta_2)S'_3$ .

(6) is 44.73 =  $\nu_1 + .62$  behind (8). If linked, it requires also  $\delta_1$  on the limit and is  $b.(-3\delta_1)S'_3$ ; if displaced  $-\Delta_1$  on the  $S_3$  it shifts 44.23 or .50 too little. The former is therefore adopted. It will be seen that both the  $S'$ ,  $S''$  hypotheses work in well with linked and displaced lines. The  $S''$  show more definitely small displacements, but are weak in explaining the exact  $\nu_2$  at (7, 8). The  $S'$  theory has to impose a definite obs. error on one line. It then forms a well-connected system, with a definite triplet; but it is difficult to explain why what should be the strongest line thereof has not been observed directly in the laboratory. The failure to discriminate between the two theories is due to two causes:—(1) the appearance of links, these being independent of the line origins; (2) the coincidence that the calculated  $S'_1$  and  $S''_1$  are separated about  $\nu_1 + \nu_2$ , so that one comes at the beginning of a triplet and the other at the end.

The parallel  $D'$  would be at 29753.48 if  $(2) + .32 = S'$ . The nearest observed line is 29742.68 at (2) in the second list. It is separated from the supposed  $D'_1$  by 10.80 or  $10s - .07$ , so that (2) may be related by displacement on the limit alone.

The D list contains the lines from  $\lambda = 3366.361$ . The shifts per oon on the limit are 1.0971 for  $D_1''$  and 1.0858 for  $D_1'$ . These lines are quite beyond the reach of any series with a  $p_1$  limit. The appearance therefore of a large number of separations near the  $\nu_1, \nu_2$  of that limit (see D diagram above) can only be accounted for by their entrance as links. We have taken (7) as  $(-\delta)D_1''(4)$ .

(9) is 45.19 =  $\nu_1 + 1.08$  ahead, *i. e.* a  $b$  link and a  $\delta_1$  displacement or  $d_1$ . It is therefore  $(-5\delta_1)D_1''b$ .

(10) is 14.54 or  $\sigma_1 + .32$  ahead, where  $\sigma_1$  is the D separation 14.22 and cannot serve. But as a  $d$  link (44.36) to (7) it gives  $44.36 + 14.22 + 1.097 = 59.68$  to meet the observed 59.73. Hence it is  $(-5\delta_1)D_2''d$ .

(3) is 45.09 behind (7). The  $a$  link is 43.99, and a  $\delta_1$  shift gives 45.09 exact. It is therefore  $a.(-3\delta_1)D_1''$ .

(4) is 7.53 ahead of (3).  $12\delta_1$  on  $p_1$  shifts 7.545;  $7\delta_1$  on  $d_1$  shifts 7.68. As  $p_1$  occurs in the  $a$  link of (3) the  $12\delta_1$

shift might be thus accounted for, but we have no experience in this connexion. The  $7\delta_1$  shift is 7.60 on  $d_1'$  and would fit, but we have found no other  $d'$  relations. The  $7\delta_1$  shift = 7.68 on  $d^n$  is excessive, but it fits to a previous  $b$  instead of  $a$  (shift 7.65). It is thus  $b(-10\delta_1)D_1^n$ .

The appearance of the separations 36 involves in both cases the explanation for the two separations 9.0. Clearly  $\phi$  displacements are involved. We need not extend the discussion. The important point for our present purpose is not a true allocation, but the fact that a consistent allocation is possible on established lines involving both  $D_1$  and  $D_2$  provided the triplet system is an independent one.

For  $m=5$  the formulæ give  $S_1^n(5)=20722.76$ ,  $S_1'(5)=20589.40$  with the own shift on  $\phi(5)=0.355$ . The list, starting from  $\lambda=4862.261$ , is long, so as to include the regions round both  $S'$  and  $S^n$ , which are now much farther apart than in  $m=4$ . Again we find the excess of separations near  $\nu_1, \nu_2$  (see diagram), and at the same time a large number of own shifts\*. It is to be noticed that (16) shows none of these. This is as it should be since (16) is  $S_1'''(2)$ , where the own shift is 1.38. Further, none of the other lines show multiples of this 1.38, in other words no limit displacements of  $S_1'''(2)$  occur. This also is in accordance with experience, as the lower orders of a series are little subject to this effect. It will be seen that the multiple shifts, as shown, afford little discrimination between the two hypotheses, since where the larger separations occur, both hypotheses exclude them. There is a possible exception with (13)–(12)=8.68, but here (13) is by a different observer.

On the  $S^n$  hypothesis, the calculated  $S_1(5)$  falls between (15, 16), but from the discussion on  $S(4)$  we were led to expect a somewhat smaller value. In fact the evidence at once points to (14) as close to the true  $S_1$  because it has a  $\nu_1$  forward, is the centre of numerous links, and especially because there is a line, (7) list D, 10966.82=C–.93, ahead to represent  $D_1(5)$ . The defect .93 cannot be explained by a displacement on one line only. But if the two observed lines be  $(2\delta_1)S_1$  and  $(2\delta_1)D_1$ , the separation of  $D_1, S_1 = 31678.23 + 2.194 - (20711.41 + 1.257) = 10967.757$ , the true C. We shall take then (14) as  $(2\delta_1)S_1$ .

\* These are calculated as on lines wholly displaced from the initial line. They will be modified where links enter.

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(19) is  $42.84 = \nu_1 - 1.27$  ahead and  $2\delta_1$  shifts  $1.26$ ; it is therefore  $(\delta)S_2$ .

(21) is  $44.94 = \nu_1 + .83 = d + .58$  ahead of the last, where the  $d$  link is  $44.36$ . It is therefore  $(3\delta_1)S_2.d$ .

(18) is  $36.96$  ahead of (14). A  $-\Delta_2$  displacement on  $p_1$  shifts  $35.70$  and the excess is now  $1.26$  or a two own shift. It is therefore  $(-\Delta_2)S_1$ .

(13) is  $48.49 = \nu_1 + 4.38$  behind (14) and  $7\delta_1$  shifts  $4.40$ . Thus we have a  $b$  link back and  $7\delta_1$  on limit, or the line is  $b.(9\delta_1)S_1$ . or since another observer is here involved it may be  $(\Delta_1 + 9\delta_1)S_1$ .

(13, 12, 11, 9) are mutually displaced as shown in the list, i.e. they are respectively  $b.[23\delta_1, 27\delta_1, 51\delta_1]S_1$ . As  $\Delta_2 = 57\delta_1$ , the last may be written  $b.(\Delta_2 - 6\delta_1)S_1$ .

(8) is  $43.97$  behind (13). The separation is practically the exact link  $a = 43.99$ . It is therefore  $a.b.(9\delta_1)S_1$ .

(7) is shown as  $41s - .22$  behind (8). But if (8) is as just determined, the shift is directly on  $S_1$  and then  $41s = 25.79*$ . Thus (7) is  $a.b(50\delta_1)S_1$ .

(5) is  $8.62$  behind, and the own shift on  $(50\delta_1)S_1$  is  $.6270$ , so that  $14s = 8.78$  and probably inadmissible.

(15) is  $-9\delta_1$  on (14) and is  $(-7\delta_1)S_1$ .

(20) is  $79.33 = \nu_1 + \nu_2 - .65$  ahead of (15), i.e.  $S_1$  changed to  $S_3$  and a  $+\delta_1$  displacement. It is  $(-6\delta_1)S_3$ .

(16) shows no mutual own shifts, as it should not, since it is  $S_1'''(2)$ .

There are few lines in the D region. (1) is another of Rowland's lines seen in the sun, and observed by no one else. (2) is  $S_2'''(3)$ . It shows a just possible own multiple shift to (4), where  $11.22 = 8 \times 1.3911 + .09$ , but doubtful. It would be  $(-8\delta_1)S_2'''(3)$ . (6) has been allocated above to  $(2\delta_1)D_1^n$ . (3.5) show the  $\sigma_1$  separation of this series, viz.  $:-14.15 = \sigma_1 - .07$ . As (3) is  $43.65$  behind (6) it suggests a  $\nu$  link or a  $40\delta_1$  displacement on (6) which gives a shift  $= 43.86$ . But in either case a simultaneous displacement in  $\phi$  is required, viz.  $:-a.(2\delta_1)D(10\delta_1)$  or  $(42\delta_1)D(-6\delta_1)$ , if the observed lines have no error. It is denoted in the list as  $a.(2\delta_1)D_1?$ , making (5) therefore  $= a.(2\delta_1)D_2?$  Then (4),  $2.22$  ahead, means the annulment of the  $2\delta_1$  displacement and is  $a.D_1^n?$ . Further (7) — an E. H. line — is  $58.99$  ahead of (6) and  $d + \sigma_1 = 58.59$ . An error  $d\lambda 2.04$  as between E. H. and Fritsch is quite possible. This would make (7)  $= (2\delta_1)D_2^n.d$ . (8) would be  $10.93$  ahead of the corrected (7) and would be accounted for by  $\sigma_2$  and the annulment of the  $2\delta_1$  displacement, viz.  $:-8.70 + 2.19 = 10.89$ . Thus (8)  $= D_3^n.d$ . For our present purpose the important point

is that we here find the  $\sigma_1$ ,  $\sigma_2$  separations appearing in possible allocations on the independent and not on the singlet hypothesis for (3) is too far ahead of (1)—given below as a possible D' line—to bring them within the singlet ambit.

On the S' hypothesis, judging from the case of  $m=4$ , we are to expect a line close to and somewhat larger than the calculated value. We find this at (6) or (7) with a  $\nu_1$  forward and a D' line at 1 in list D about C ahead. This last line is another of Rowland's sun lines, and observed by no one else. The separations from (6, 7)=10972.40, 1.61 are C+4.65, +3.86, while (6, 7) are decisively not mutual limit collaterals. The excess 4.65 has no obvious relation to our shifts, but 3.86=.62+3×1.08, or exactly one our displacement on S' and three on D'. But the exactness again must be a pure coincidence since the lines are measured by different observers. Taking this indication however, (7) in S is  $(-\delta_1)S'_1$  and (1) in D is  $(3\delta_1)D'$  or  $S'_1(5)=20593.70$ ,  $D'_1(5)=31561.45$ . The excess 4.30 over the calculated is larger than we should expect, compared with .46 for  $m=4$ . (9) in S is 43.73 ahead of (7). This has no reference to a displaced  $S'_2$  line unless the  $S_2$  has displacement also in the  $\phi$  term. Numerically it is 44.36-.63 or the  $d$  link with  $+\delta_1$  on limit, i.e. is  $S'_1(5).d$ . without any displacements. But if so there is no allied  $S'_2$  seen.  $(7)-(5)=8.62=14s-.06$  or a 14 our displacement on S' basis and probably not on S<sup>n</sup> basis. Thus  $(5)=(13\delta_1)S'_1$ . There is definitely no connexion with (8). There is nothing to be gained by following up the connexions further. Comparing the two theories we find

$$\begin{array}{l} (2\delta_1)S_1^n \quad (2\delta_1)D_1^n \quad \left| \begin{array}{l} (-\delta_1)S'_1 \quad (3\delta_1)D'_1 \\ (\delta_1)S'_2 \quad (?)S'_2(?)=S'_1.d \end{array} \right. \\ (-6\delta_1)S_3^n \quad (2\delta_1)D_2^n . d \quad D_3^n . d \end{array}$$

with a doubt as to the real existence of the D' line.

Although the discussion of the "singlet" data affords good illustrations of the displacement effect, it unfortunately does not give any clear and certain discrimination between the two hypotheses as to the nature of these series, although perhaps on the whole it favours that of independent origin. The reason for this is that the links have the same value on either hypothesis, and that the two limits, 24189, 24405, are so close that the shifts per our on them are very nearly the same for the same wave-number. Differences in multiples of these shifts therefore only become greater than possible observation errors when these multiples are very large.

But we have met with one possible criterion which may be found to weigh heavily against the singlet hypothesis. This is the allocation of lines for  $S'(4)$  and  $D'(5)$  which have been observed by Rowland when identifying the origin of very faint lines seen by him in the sun, and seen by no other observer. If the existence of these lines as due to Mn is established we get a very strong support for the singlet theory, especially as a complete triplet would then be found for  $S'(4)$ . If after a special search no such line can be found, the argument against this theory would become very strong.

The own relations, (see III.) while favouring the singlet hypothesis where the two multiplet terms  $\phi_1, \phi_2$  are concerned, are decisively against it, in connexion with the triplet separation sum, 79.98, if these new terms are subject to the same rules as those obeyed by the hitherto known terms. It would seem that the question of the nature of these new series must remain open for the present.

XXXV. *Observations on the Note of Dr. L. Silberstein: Determination of the Curvature Invariant of Space-Time* (Phil. Mag. xlvii. 1924, pp. 907-917). By H. WEYL, Professor a. d. Eidg. Techn. Hochschule, Zuerich\*.

1. DR. SILBERSTEIN maintains (footnote, p. 909) that "tan" ought to stand for "sin" in my formula for the displacement to the red  $\tau$ , for this is the result furnished by his own formula (5, p. 912) for  $\gamma=1$ . But in my case  $r$  signifies the distance of the star measured in the static space of the observer at the moment of observation. For Dr. Silberstein, on the contrary,  $r$  signifies a very artificial (in some instances complex-imaginary) quantity—namely, the distance of the star from the observer at the moment of observation, but in the static space of the star.

2. I have by no means "more or less disguised as a necessary feature of de Sitter's world" the assumption regarding the world-lines of stars. On the contrary, going further than de Sitter and Eddington, I strongly emphasized the necessity for adding an assumption regarding the "undisturbed state" of stars, if anything in the theoretical line regarding the displacement to red is to be formulated. The hypothesis also which I have pursued arithmetically is not "perfectly gratuitous," but simply means that the stars of

\* Communicated by the Author.

† *Raum Zeit Materie*, 5. Auflage, Berlin, 1923, p. 323; *Physikalische Zeitschrift*, xxiv. p. 230 (1923).

the system are able to act upon one another from eternity. Another hypothesis has been followed by Mr. K. Lanczos\*, but mine has the great advantage of not introducing a singular initial moment, of conserving the homogeneity of time. (Moreover, it is the only one which satisfies this requirement.) However, the cosmology arrived at in this way remains also for me—that is self-understood—an hypothesis, even a rather daring but nevertheless reasonable hypothesis.

3. Curiously enough, Dr. Silberstein at the end of his articles uses exactly the same assumption as a basis, the only difference being that he adds to my group of world-lines, which diverges into the future, that which results from it through the interchange of past and future (double sign). That, I must confess, appears quite abstruse to me. If (according to the opinion of van Maanen and Shapley) the conception which has been developed by Charlier, Lundmark and others is erroneous—the conception, namely, that the spiral nebulae are extra-galactic and in consequence a good deal further off than the other heavenly bodies, including the globular clusters,—then, of course, the cosmological interpretation of that pronounced displacement to the red which the spectrum-lines of the greater majority of them show becomes impossible.

Zuerich, 15 June, 1924.

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XXXVI. *The Electrical Conductivity and certain other Properties of Metals and Alloys on the Basis of Bohr's Theory.*  
By KRISTIAN HÖJENDAHL, *Danish Government Ramsay Memorial Fellow* †.

*Introduction.*

**M**ETALS and alloys form an outstanding group of bodies possessing certain characteristic properties. Theoretical explanations of these properties have already been put forward by various authors.

In this paper the attempt is made to show to what extent such properties can be accounted for on the basis of the rotation of the elliptic orbit of the valency electron, which, according to Bohr ('Nature,' vol. cxii. p. 29, 1923), is much more pronounced for the case of metals than for hydrogen. The reason for this rotation is that the field-force is stronger

\* *Zeitschrift für Physik*, xvii. pp. 168-189 (1923).

† Communicated by Prof. W. C. M. Lewis.

inside the inner electron shells than it is outside. In passing from lithium to carbon in the periodic system, the difference between the inside and the outside of the K shell diminishes; and it can therefore be understood why the rotation of the elliptic orbit can be overcome in the case of carbon atoms chemically bound, whilst this is not the case for lithium.

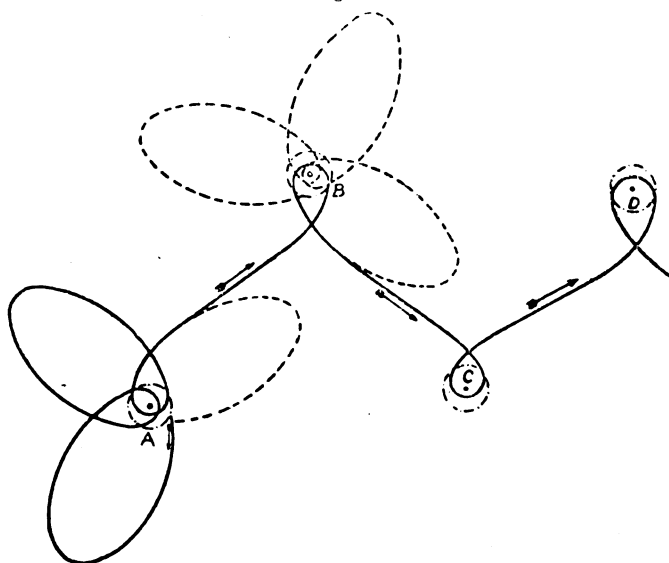
The "shared" electrons constituting a typical organic (covalent) bond are assumed to move in shared orbits similar to the figure of eight proposed by Sidgwick (Trans. Faraday Soc. vol. xix. pt. 2, p. 469, 1923). The shape of a loop in a figure of eight is very similar to that of the inner loop in an elliptic orbit with a small rotation. This analogy might also be expected for the following reason. Near to one atom the influence of other atoms on the orbit of an electron must be small. The electron, therefore, will move very nearly in the same path as it would if the other atoms had been absent—that is, in the free atoms. This agrees with the view expressed by R. H. Fowler (Trans. Faraday Soc. vol. xix. p. 459, 1923), who assumes that the loop of a shared orbit in a (compound) molecule may replace and represent the inner part of an unshared orbit in an isolated atom.

### *The General Structure of a Metal.*

The manner in which electrons possessing considerable orbital rotation can form covalent bonds between pairs of atoms may be illustrated as follows. Let us take 2 atoms of vaporized lithium (A and B in fig. 1). Only the orbit of the valency-electron originally belonging to one of the atoms, namely A, is considered. It describes a rosette round A, as shown in the figure. When an outer loop comes close to B, it may happen that the attraction from B on the electron will be so strong that it will balance that from A, and the electron will therefore move in a straight line towards B. Near B the field of B is the dominating one. The electron therefore moves round B in nearly the same way as does an electron in a free atom—*i. e.*, in the dotted rosette. It will be realized that the electron, when moving in the rosette, will not be expelled into the sphere of attraction of A before it has passed the whole way round in the rosette. Only for the time-interval during which the electron is passing between the atoms can these be considered as bound together with a covalent bond. This happens only at intervals, and consequently the bond in this case is not a stable one, and metallic vapours are practically monatomic.

If, however, the liquid or solid state is considered, there will be a third atom C and a fourth atom D relatively close to A and B, as shown in the diagram. If this is the case, the electron, when expelled from B, may be caught by C traversing a *rosette-shaped* path around it, and then in turn may be captured in a similar manner by D, and so on in a zigzag path throughout the metal.

Fig. 1.



For the case of a crystalline metal the atoms are arranged in a space-lattice. The zigzag paths of the electron, therefore, will be very regular and placed in a number of equivalent directions. The atoms are thus knitted together in many directions by electronic orbits. Electrons follow rapidly in the same path at definite intervals. Every time an electron passes over between two atoms, these may be considered as bound together with a covalent bond. When a crystal of a metal is disintegrated, such bonds must be broken. Similar bonds are not broken by the disintegration of other crystals. Thus the bonds, which are broken in the case of a crystal consisting of organic molecules, are those weak attractions, due to polarity only, which join the molecules together. Such molecular attractions are not due to covalency, as envisaged above. The bonds broken in the case of a salt are the electrostatic

attractions between the ions. In non-metals, only in a few cases such as the diamond are actual covalent bonds broken. It should be emphasized that the passage of the "covalent" electrons here considered, although involving translations from place to place, is wholly different from the old and now-discarded theory of freely-moving electrons. The motion here considered is a quantized one.

Another comparison between crystalline substances is suggestive—namely, that the heat-conductivity is high in all cases where electrons pass over in quantized paths between the atoms as in the case of the diamond and the metals; whilst for the cases of salts and organic crystals, where such transitions do not take place, the heat-conductivity is low. It must therefore be assumed that the energy of the electrons varies (very slightly) with temperature. The valency-electrons, however, do not possess measurable heat-capacity, since their characteristic quantum energy is supposed to be very high. The marked conductivity is due in part to the *rapidity* of motion of the valency electrons.

The quantum energy of the valency-electron arises because the zigzag path of the electron represents the path of an oscillator, which moves from one atom to its neighbour for one vibration. This means that the shape and dimensions of the path, and the velocity, energy, and frequency of the electron, approximate (closely) to definite values. Thus also the dimensions of the crystal-lattice are fixed. The crystalline form which the metal takes up is determined mainly by the angle of rotation ( $\phi$  in fig. 2). The definite state, however, only appears at the absolute zero. At higher temperatures the vibrations of the atoms will be superimposed on the motion of the electrons, and cause slight changes in the total energy of the electron and in the dimensions of the crystal. The change in the total energy of the electron is the ultimate cause of heat-conduction.

#### *The Electrical Conductivity of Pure Metals.*

It is evident that the system outlined above will be an excellent conductor for electricity. In its consequences it is similar to a theory of Wien (*Berl. Ber.* vol. vii. p. 184, 1913); in fact, it gives a model for Wien's theory. Wien's treatment is based on Drude's equation:

$$\sigma = \frac{1}{2\pi u} e^2 N L, \quad . . . . . (1)$$

where  $\sigma$  is the specific conductivity,  $u$  the *mean velocity* of

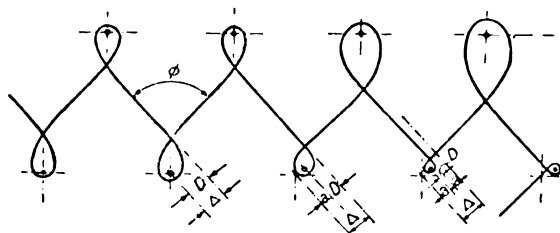
the electron and  $e$  its charge,  $L$  the mean free path, and  $N$  the number of free electrons in 1 c.c.

Wien assumes that  $u$  and  $N$  are constant ;  $L$  is the only temperature variable that remains. Furthermore, Wien assumes that the path of an electron is changed abruptly by vibrating atoms only, and that the probability of an abrupt change is proportional to the square of the amplitude of the atom. Introducing Debye's theory, he arrives at the following equation for the specific resistance :

$$w_T = C \frac{kT\nu_m}{h} (1 - \frac{1}{4}\rho_m + \frac{1}{36}\rho_m^2 - \frac{1}{3600}\rho_m^4), \quad (2)$$

where  $\rho_m = \frac{h\nu_m}{kT}$  and  $\nu_m$  is the maximum frequency. The equation is in good agreement with experiment. The resistance vanishes before the absolute zero is reached, and the temperature-coefficient for normal temperatures becomes somewhat larger than  $1/273$ . A basis for Wien's assumptions is found in the present model. As has already been shown, the velocity of an electron is constant. Also, as shown in fig. 2, the actual zigzag path pursued constitutes, owing to its persistence, an effective linear motion in one direction—i. e., parallel to a row of atoms. This would go on indefinitely, if all the atoms were at rest and of the same kind, and thus give rise to the superconductivity at absolute zero. If, however, one of the atoms is displaced, the path will be disturbed in the way shown in fig. 2, and if the displacement is large enough, the path will be abruptly changed in direction by a definite characteristic angle in the crystal. Even if the effect is not due to a single atom, the disturbances of the path caused by several displaced atoms will sum up and finally cause an abrupt change in direction,

Fig. 2.



as shown in fig. 2. The new effective direction pursued by the electron will be parallel to another row of atoms in the crystal. The mean length of the "unbroken" path between



two such abrupt changes in direction is considered as being analogous to the mean-free-path in Drude's theory. A single "unbroken" path obviously consists in general of a certain number of zigzag "vibrating" movements. A single "vibration" is not to be taken as the analogue of the mean-free-path of the older view.

The degree of disturbance of the quantum path of the electron may be represented by the change in the distance  $D$  (fig. 2) between the nucleus of an atom and the tangent to the point of inflexion in the preceding branch of the electron's quantum path. The normal value of this distance is  $\Delta$ . As shown in fig. 2, the thermal displacement  $a$  of the atom is subtracted or added directly to  $\Delta$  to give the value of  $D$  at the first displaced atom. The displacement  $a$  of one atom will cause a corresponding disturbance of the electron motion at all the succeeding atoms. Whether these disturbances are larger or smaller than  $a$  depends on the nature of the field-force of the atoms. It is assumed that the disturbance of the electron caused by a displacement  $a$  of one atom will appear with the same magnitude at the succeeding atoms. When the total disturbance becomes larger than  $\Delta$ , i. e.  $D=0$ , the electron will be expelled to the "wrong" side of the last atom in the sequence, and the path will be abruptly changed in direction. The displacements of the atoms are not all to the same side, but distributed according to probability laws. The total disturbance therefore follows the rule for summation of experimental errors. Consequently, the number of atoms  $n$  which on the average are necessary for obtaining a total disturbance  $\Delta$  of the electronic path is given by the equation :

$$\Delta = \bar{a} \sqrt{n}$$

$$\text{or } \frac{1}{n} = \frac{\bar{a}^2}{\Delta^2} \dots \dots \dots (3)$$

where  $\bar{a}$  is the mean amplitude (displacement) of the atoms.

The above equation (3) shows, in agreement with Wien's assumption, that  $\frac{1}{n}$ , the probability for "break" or abrupt change of the path of an electron, is proportional to the square of the amplitude of the atom.

It follows from this that the probability of a "break" is (approximately) proportional to the heat-energy of the atom; this means in turn that the magnitude of the resistance is proportional to the heat-content. At sufficiently high

temperature the heat-content becomes proportional to the absolute temperature. Hence also the resistance becomes proportional to the absolute temperature.

### *The Electrical Conductivity of Alloys.*

A more marked disturbance, *i. e.* a more frequently occurring effect, may appear in the path of an electron when an atom in the crystal is replaced by an atom of another kind. The foreign atom necessarily alters the characteristic angle  $\phi$ , with the result that the effective direction of the path of the electron is abruptly changed, generally at the foreign atom.

The resistance  $R_0$ , which arises in this manner, depends on the heterogeneity introduced; the alloy-resistance  $R_0$  persists at the absolute zero, and is practically a constant for all temperatures. In addition to the above effect, the heat-vibrations also will cause "breaks" (abrupt changes in direction) in the normal way, and give rise to a certain resistance  $R_T$ , which depends on temperature in the known manner. From what has been said already, it follows that at  $0^\circ \text{C.}$  the temperature-coefficient with respect to  $R_T$  alone is

$$\frac{1}{R_T} \cdot \frac{dR}{dT} = \text{circa } \frac{1}{273}.$$

With respect to the total resistance of an alloy, the temperature-coefficient becomes

$$\frac{1}{R_0 + R_T} \cdot \frac{dR}{dT} = \frac{1}{273} \cdot \frac{R_T}{R_0 + R_T} \cdot \cdot \cdot \cdot \cdot \quad (4)$$

For ordinary alloy-compositions,  $R_0$  is generally much larger than  $R_T$ ; hence it will be seen that the temperature-coefficient of alloys (mixed crystals) is small. If  $R_T$  is the linear mean of the resistances of the components, the above expression is identical with the empirical expression given by Matthiessen, as cited by Guertler (*Jahrb. Radio-Elekt.* v. p. 17, 1908).

If it be assumed that the electron-path is always "broken" (abruptly changed in direction) at a foreign atom, an expression for the relation between the composition of the alloy and the specific alloy resistance  $R_0$  may be obtained in the following manner.

Let us consider the probability  $p$  that the path of any electron shall be "broken" or not "broken" at any atom

in a mixture of  $a$  atoms of a metal A and  $b$  atoms of another metal B. The condition that a "break" shall occur is that the preceding atom shall be of another kind. The sequences  $B-\overset{\times}{A}-B$  and  $A-\overset{\times}{B}-A$  will give "breaks" at the crossed atoms, and therefore not at the last ones.  $B-B-\overset{\times}{A}$  and  $A-A-\overset{\times}{B}$  will give a "break" on the last atom. The probabilities that the atom considered shall be the last one in a sequence of the latter type are

$$\frac{ab^2}{(a+b)^3} \text{ and } \frac{a^2b}{(a+b)^3} \text{ respectively ;}$$

$$\text{total probability} = \frac{ab}{(a+b)^2}.$$

These are the most predominant, but not the only combinations, which lead to a "break" on the last atom; others are  $(B\overset{\times}{B}\overset{\times}{A}\overset{\times}{B}\overset{\times}{A})$  and  $(A\overset{\times}{A}\overset{\times}{B}\overset{\times}{A}\overset{\times}{B})$  and  $(B\overset{\times}{B}\overset{\times}{A}\overset{\times}{B}\overset{\times}{A}\overset{\times}{B}\overset{\times}{A})$  and  $(A\overset{\times}{A}\overset{\times}{B}\overset{\times}{A}\overset{\times}{B}\overset{\times}{A}\overset{\times}{B})$  etc., with the probabilities

$$\frac{a^2b^3}{(a+b)^5} + \frac{a^3b^2}{(a+b)^5} = \frac{a^2b^3}{(a+b)^4},$$

$$\frac{a^3b^4}{(a+b)^7} + \frac{a^4b^3}{(a+b)^7} = \frac{a^3b^3}{(a+b)^6}.$$

The total probability  $p$  that the path shall be "broken" at any atom is given by the sum of the progression :

$$p = \frac{ab}{(a+b)^2} + \left[ \frac{ab}{(a+b)^2} \right]^2 + \left[ \frac{ab}{(a+b)^2} \right]^3 + \dots = \frac{\frac{ab}{(a+b)^2}}{1 - \frac{ab}{(a+b)^2}}.$$

The average distance  $L$  (in lattice spacings) between two consecutive "breaks" (or abrupt changes in direction)—which distance, on the old view, would be the mean-free-path of the electron—is given by the inverse of the expression for  $p$ . That is,

$$L = \frac{1 - \frac{ab}{(a+b)^2}}{\frac{ab}{(a+b)^2}} \quad \dots \quad (5)$$

According to Drude's equation (equation 1),

$$R_0 = \frac{2mu}{e^2N} \cdot \frac{1}{L} \quad \dots \quad (6)$$

Inserting the expression for  $L$ , denoting the atomic fraction  $\frac{a}{a+b}$  by  $c_1$  and  $\frac{b}{a+b}$  by  $c_2$ , and putting  $\frac{2mu}{e^2N}$  equal to  $C$ , the following expression is derived :

$$R_0 = C \cdot \frac{c_1c_2}{1-c_1c_2} \quad \dots \quad (7)$$

$C$  is only a constant in so far as the velocity  $u$  is the same for the two metals.

The above relation is very similar to an empirical relation given by Guertler (*Jahrb. Radio-Elektr.* v. p. 17, 1908), namely

$$W_2 = CK(100-K),$$

where  $W_2 = R_0$  ;  $K$  is volume-percentage, and  $C$  a constant. He obtains a good agreement for the alloy Ag-Au (where atomic fractions and volume-percentage are proportional). In the following Table I., equation (7) has been tested on the experimental values for the alloys Cu-Ni given by Feussner (*Landolt-Börnstein*, 5th ed. p. 1054). In this case also, volume-fractions are equal to atomic-fractions. The temperature-resistance  $R_T$  is taken as the linear mean of those of the components, employing the familiar "mixture law" formula.

TABLE I.

Volume per cent. nickel.	Atomic fraction.	Total resistance.	$R_T$ .	$R_0$ .	$C = \frac{2mu}{e^2N}$ .
0.0	0.000	16.2	16.2	0.0	
10.5	0.105	149.0	27.4	121.6	1170
20.8	0.208	266.4	38.3	228.1	1156
25.0	0.250	316.2	42.7	269.5	1163
31.0	0.310	392.2	48.2	344.0	1260
41.0	0.410	488.0	59.7	428.3	1340
51.2	0.512	540.0	70.6	459.4	1380
63.0	0.630	500.0	83.0	417.0	1375
92.8	0.928	185.0	115.0	70.0	980
96.6	0.966	165.0	119.5	46.0	1540
100.0	1.000	122.5	122.5	0.00	

The table shows as good a constancy for  $C$  as can be expected in view of the variation in  $u$ .

If actually the path of every electron is "broken" every time it arrives at a foreign atom, the rise in resistance caused by introduction of a small amount of another metal ( $B$ ) may lead to a determination of the distance between two

consecutive abrupt changes in the effective direction of the path or, as it also may be termed, the mean length of the "unbroken" path of the electron in the pure metal A. For this case ( $c_1$  small) the above equation gives

$$R_0 = \frac{2mu}{e^2 N} \cdot \frac{c_1 \times 1}{1}.$$

The total resistance is this plus the temperature-resistance  $R_T$ , which is the same as that for the pure metal A. According to equation (1),

$$R_T = \frac{2mu}{e^2 N} \cdot \frac{1}{L}.$$

The velocity  $u$  is the same for the pure and the impure metal, and consequently for the metal A:

$$L = \frac{1}{c_1} \cdot \frac{R_0}{R_T} \text{ lattice-spacings.} \quad . \quad . \quad . \quad (8)$$

Now consider another alloy of the metal A—namely A mixed with C. If an atom of C "breaks" the path of an electron at every collision therewith, the mean length of the "unbroken" path calculated on the basis of the A-C alloy should give the same result as that calculated on the basis of the A-B alloy. This actually seems to be the case, as shown below in Table II. The experimental data are mainly taken from a diagram in Guertler's paper (*l. c.*).

TABLE II.

Resistance of iron with 2 weight-percent of other metals.

Mean length of "unbroken" path in iron.

	Atomic fraction.	Total resistance.	Resistance of iron.	$R_0$ .	L calculated from Guertler & Matthiessen's data.	L calculated from other investigators' data.
W .....	0.006	119	76	43	72.0	
Au.....	0.0057	139	...	63	110.0	
Ni .....	0.019	161	...	85	44.7	
Cr .....	0.0214	192	...	116	54.2	
Mn ...	0.0203	210	...	134	66.0	50
Si .....	0.0394	335	...	259	66.0	63 : 67
Al .....	0.0413	370	...	294	71.3	58
C .....	0.0930	660	...	584	63.0	
Cu.....	...	...	...	...	...	42

Gold seems to be the only exception in so far as the value for it is definitely outside the experimental error, which is very large. The mean length of "unbroken" path for the valency-electron in iron is about 60 lattice-spacings—i. e., about  $1.7 \times 10^{-6}$  cm.

In the same manner the mean length of the "unbroken" path of (probably impure) platinum is found to be about 8 lattice-spacings.

For solid mercury  $L$  is about 9, based on mercury-sodium alloy. If this is the correct value, the mean length of the "unbroken" path in liquid mercury will only be about 2 lattice-spacings if the same proportionality holds for the liquid as for the solid state.

When the mean length of the unbroken path has been determined in this manner, the velocity of the electron may be determined by help of equation (6)—viz.,

$$R = \frac{2mu}{e^2 N} \cdot \frac{1}{L}.$$

Inserting the value for iron, a velocity of the order  $4.3 \times 10^8$  is obtained. As might be expected, it is of the same order as the velocity of an electron in a hydrogen atom.

Taking the lattice-spacing as  $2.83 \times 10^{-8}$ , the vibration-frequency of the electron considered is  $1.5 \times 10^{16}$ —i. e., a quantity so large that any energy term dependent upon it would be negligible in specific-heat measurements.

#### *Summary.*

1. On the basis of the Bohr atom, with special reference to the rotation of the orbit, the attempt has been made to envisage the formation of a *di-atomic* compound in a metallic vapour by the sharing of electron orbits. A permanent diatomic compound cannot be formed, and in the state of vapour the metal must be monatomic. It is, however, possible to form an infinite-atomic compound (the metallic state). In this an electron does not move inside a limited space; but it moves in a quantized zigzag path throughout the metal.

2. The shape of this path, the distances between the atoms, and the energy and velocity of the electron will be determined by quantum rules. Hence they will be only slightly dependent on temperature.

3. In a perfect crystal at the absolute zero the paths will be regular, of the same length as the crystal, and placed in a number of equivalent directions parallel to rows of atoms. The direction of the path may be abruptly changed, i. e. "broken," by (a) the heat-vibration of the atoms, by (b) irregularities in the crystal, and (c) by introduction of atoms of another kind.

4. The "unbroken" path is the analogue of the free-path in Drude's classical theory. The specific electrical conductivity, then, is proportional to the mean length of the "unbroken" path.

5. The present model provides a basis for the assumptions underlying the theoretical treatment of Wien on the relation between electrical conductivity and temperature.

6. It indicates why alloys have a high resistance and a low temperature-coefficient. A theoretical expression for the relation between resistance and composition of a perfect mixed crystal is worked out in fair agreement with experiment.

7. The rise in resistance caused by introducing 1 atom of a number of metals into 100 atoms of a pure metal (A) is nearly constant for the same pure metal. This leads to a determination of the mean length of the "unbroken" path in metal A expressed in lattice-spacings

8. On this basis the velocity of the covalent electrons in iron has been calculated, using Drude's equation. The calculated velocity is of the right order of magnitude.

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XXXVII. *The Band Spectrum of Mercury and the Dissociation of Hydrogen Molecules by Excited Mercury Atoms.*  
By K. T. COMPTON, *Ph.D., D.Sc., Professor of Physics*, and  
LOUIS A. TURNER, *M.A., Ph.D., Charlotte Elizabeth Procter  
Fellow in Physics, Princeton University* \*.

IT has long been known that an electric discharge of low intensity in mercury vapour causes the appearance of a band spectrum. In addition to the green and ultra-violet unresolved bands, prominent in the fluorescent spectrum and ascribed to  $\text{Hg}_2$  molecules formed in the presence of excited atoms †, there have been found several bands with resolvable structure ‡. The earlier workers found that these bands were enhanced in intensity when a stream of vapour was maintained in the discharge-tube by evaporating mercury at one end and condensing it at the other. The heads of the most intense bands are of wave-lengths 4219, 4017, and 3728. They shade off toward the short wave-length side, and are made up of comparatively easily resolvable lines of which the wave-lengths were measured by Liese §. Bands of similar structure have also been found in the spectra of zinc and cadmium. These band spectra have been analyzed by Hulthen ||, who came to the conclusion that the emitters of these spectra must be molecules composed of heavy metal atoms and atoms of an element of low atomic weight, since the wide spacing of the lines

\* Communicated by the Authors.

† Franck and Grotrian, *Zeits. f. Phys.* iv. p. 89 (1921).

‡ Kayser, *Handbuch der Spektroskopie*, vol. v.

§ E. Liese, *Zeit. wiss. Phot.* xi. p. 349 (1912).

|| Erik Hulthen, *Zeit. für Physik*, xi. p. 291 (1922).

indicates a small moment of inertia of the molecules. He suggested a nitrogen compound as a possibility, owing to certain simultaneous variations of intensity of these bands and those of nitrogen, when the conditions of excitation were varied. Kratzer\* analyzed these spectra also, revised Hulthen's arrangement somewhat, and came to the conclusion that the emitters must be molecules of a hydride rather than of a nitride, since their moment of inertia is less than that of a nitrogen molecule. Mulliken† has recently pointed out that these bands show no evidence of separations due to the different isotopes of the metals, and has shown that this fact favours the theory that the bands are emitted by hydride molecules.

We have obtained experimental results of a different kind, which confirm this theory that the band spectrum of mercury is emitted by molecules of a mercury hydride. We have taken photographs of the spectrum of the light emitted by the positive column of a Geissler discharge in a tube with a tungsten filament cathode, containing mercury vapour at a pressure of 0.3 mm. and hydrogen at different pressures from 0.16 mm. down, with 80 volts applied to the anode. The band spectrum is quite strong in comparison with some of the lines of medium intensity in the mercury spectrum at the higher pressures of hydrogen, and is almost entirely gone when the hydrogen is pumped out by a diffusion pump. Its strength is roughly proportional to the hydrogen pressure. This we consider to be a good indication that the bands are due to the hydride of mercury. This experiment is somewhat of a confirmation of the quantum theory of band spectra, since Kratzer's calculation of the moment of inertia of the molecule was based on that theory. This experimental arrangement gives a good source of the light of this band spectrum, which should be of use to anyone with the proper spectroscopic equipment who might wish to extend our knowledge of this spectrum by a study of the structure of some of the weaker bands. Apparently the evaporation and condensation of the mercury in the earlier experiments caused the production of hydrogen in the tube which would otherwise have remained dissolved in the liquid mercury.

The question arises as to whether this spectrum is emitted following the excitation of mercury hydride molecules existing in the tube, or whether these molecules form by the reaction of hydrogen with excited mercury atoms. We believe that the latter process is the one which occurs. W. H. McCurdy has made an extensive study of the discharge in mercury vapour in a tube of this sort. He found that the positive

\* A. Kratzer, *Ann. der Physik*, lxxi. pp. 9-12, 72 (1923).

† R. S. Mulliken, 'Nature', cxiii. p. 489 (April 5, 1924).



column was uniform when the mercury vapour was pure, but became striated when impurities were present. He introduced hydrogen in order to produce the striations. His measurements of the density of the electrons, their mean velocity, their velocity distribution, and the potential gradient in the striated discharge, which are to be published later, show that the bright parts of the striations are the regions where many inelastic impacts occur, resulting in the formation of mercury atoms in the  $2p_1$ ,  $2p_2$ , and  $2p_3$  states. Consideration of the mobilities of electrons of different velocities and of space-charge effects leads one to expect a striated discharge, provided that the excited atoms in the  $2p$  state do not diffuse far away from their place of formation, thus offering the possibility of inelastic collisions with electrons of almost any low velocity at any place in the tube. The function of the hydrogen is apparently the prevention of this diffusion of metastable excited mercury atoms throughout the tube by collisions of the second kind in which the energy of the excited atom is used up in dissociating the hydrogen molecule, as in the experiments of Cario and Franck\*. When the hydrogen is pumped out, the excited atoms diffuse throughout the tube and the striations disappear. According to this theory, the bright parts of the striations should be regions of high concentration of mercury atoms in the  $2p$  excited states. We have found that the subordinate series lines of mercury 5461, 4358, and 4047,  $2p_{1,2,3}-2s$ , are much more strongly absorbed in these regions than in the dark spaces between striations. This theory and these experiments will be discussed fully in another paper. We also find that the band spectrum of mercury hydride is emitted from the regions of high concentration of excited mercury atoms. This would not be the case if the emission of the spectrum resulted from the excitation of already existing hydride molecules, and did not depend upon the presence of excited mercury atoms.

Cario and Franck suggested as a possible explanation for their experimental results on the clean-up of hydrogen molecules by excited mercury atoms that the excited atom gave up its energy to dissociate the hydrogen molecule into the two atoms, the excess energy appearing as kinetic energy of the three resulting atoms. This explanation meets with difficulties, however, if we consider thermal equilibrium in a region containing hydrogen and mercury. Such considerations are analogous to those which originally led Klein and Rosseland† to the idea of collisions of the second kind. In

\* G. Cario and J. Franck, *Zeit. für Phys.* xi. p. 161 (1922).

† O. Klein and S. Rosseland, *Zeit. für Physik*, iv. p. 46 (1921).

order to maintain the equilibrium, this dissociation of hydrogen would have to be counterbalanced by the reverse process, which would be the simultaneous encounter of two hydrogen atoms and a mercury atom, resulting in the formation of a hydrogen molecule and an excited mercury atom. The colliding atoms would need to have enough kinetic energy so that its sum with the energy of combination of the hydrogen atoms would be sufficient for excitation of the mercury atom. This is a most improbable happening. The present experiments suggest an explanation which presents fewer difficulties. It is that the excited mercury atom reacts with the hydrogen molecule to form a hydrogen atom and an excited molecule of mercury hydride. This excited molecule radiates the band spectrum, and then may dissociate into a normal mercury atom and a hydrogen atom. This explanation accounts for the experiments of Cario and Franck and our experiments on the band spectrum, and offers fewer difficulties in the consideration of the thermal equilibrium. It should be pointed out that this possible different explanation of the process makes no difference in the calculation of the average life of the mercury atom in the  $2p_2$  state made by one of us\*, upon the basis of the measurements of Cario and Franck.

*Summary.*

1. The band spectrum of mercury, the heads of the three strongest bands of which are of wave-lengths 4219, 4017, and 3728, is developed strongly in a Geissler discharge in a tube containing a mixture of mercury and hydrogen, but disappears when the hydrogen is pumped out. This supports Kratzer's conclusion, based upon a study of the structure of the bands from the point of view of the quantum theory, that the emitters of the bands are molecules of a hydride of mercury.

2. The bands appear in the regions of the striated discharge where the concentration of excited mercury atoms in the  $2p$  states is greatest. This fact indicates that the presence of these excited atoms is necessary for the production of the bands.

3. It is suggested that an excited mercury atom reacts with a hydrogen molecule to form an excited hydride molecule and a hydrogen atom rather than to dissociate the hydrogen into two atoms immediately, by a collision of the second kind.

*Note added with the proof.*—An attempt was made to excite these bands optically by absorption of resonance 2536 radiation in a mercury-hydrogen mixture, but without success.

\* Louis A. Turner, Phys. Rev. xxiii. p. 464 (1924).

XXXVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xlvii. p. 784.]

March 12th, 1924.--Prof. W. W. Watts, Sc.D., F.R.S.,  
Vice-President, in the Chair.

THE following communication was read :—

‘The Old Red Sandstone of the Cardiff District.’ By  
Albert Heard, M.Sc., F.G.S., and Richard Davies, M.Sc.

This paper gives an account of an exhaustive petrological investigation of the Old Red Sandstone of the Cardiff District. During the course of the work, a new fish-band was discovered in the Red Marl Group. This Coed-y-Coedcae Fish-Bed contains innumerable fragments of *Cephalaspis* and *Pteraspis*, together with *Pachytheca* and obscure plant-remains.

The petrological investigation revealed a rich assemblage of pebbles and minerals. Among the pebbles, vein-quartz and opalescent quartz are the most abundant, with numerous acicular, irregular, and especially regular inclusions. Evidence of intense mechanical deformation is generally exhibited. Cherts, jaspers, and pebbles of quartz-gneisses, mica-schists, sandstones, and quartzites are abundant. Pebble-beds, with sandstone-pebbles not assignable to any Lower Palaeozoic sediments, are of common occurrence in the Red Marl Group. The finer constituents include quartz-grains similar to larger quartz-pebbles, abundant fresh microcline and oligoclase, and many large flakes of white mica and chlorite; fresh biotite occurs in the cornstones.

The ‘heavy’ minerals include ilmenite and leucoxene, pyrites, garnet, tourmaline, a large proportion of coloured to colourless zircons, rutile, apatite, and a little magnetite.

Three definite mineralogical zones are established, corresponding roughly with the stratigraphical groups.

The cornstones have been investigated, and partial chemical analyses made. A physico-chemical origin is suggested.

The sediments are compared with the Torridonian and Millstone Grit of Yorkshire, and it is concluded that the Old Red Sandstone of the Cardiff district represents estuarine and deltaic deposits derived mainly from a pre-Cambrian massif on the north-west.

The Silurian rocks of the Cardiff district have been investigated, and have proved to be entirely different and distinct from the Old Red Sandstone. No pebbles from the Silurian have been observed in the lowest Old Red Sandstone beds. It is concluded that the definite petrological break represents a non-sequence. The hypothesis of the ‘Welsh Lake’ is considered to be untenable.

A probable connexion with the Devonian of North Devon is suggested.

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PHILOSOPHICAL MAGAZINE  
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[SIXTH SERIES.]

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SEPTEMBER 1924.

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XXXIX. *The Complexity of the Elements.*—Part II. *Elements of Even Atomic Number* \*. By A. S. RUSSELL, M.A., D.Sc.,  
*Student and Tutor of Christ Church, Oxford* †.

§ 1. *Introduction.*

IN this paper I propose to develop a scheme for predicting the complexity of elements of even atomic number in the range  $z=82$  to 36, making use of the principles and postulates of Part I. of this paper. The possible complexity of even elements will be dealt with first, in general terms; second, an attempt will be made to arrange the mass-numbers of the isotopes of many elements in the order in which they are considered to be in Nature; and third, the relation of mass-number to the stability of the nucleus will be discussed.

§ 2. *The Limits of the Mass-Numbers of Even Elements in the range  $z=82$  to 36.*

Even elements may be considered in four groups—(1) simple elements, (2) complex elements without odd isotopes, (3) with one odd isotope, and (4) with two odd isotopes. An element of the first group has one mass-number, of the second two or three, of the third five, and

\* Part I., *Phil. Mag.* vol. xlvii. p. 1121 (1924).

† Communicated by the Author.

of the fourth seven. This is arrived at in the following way :—

- (a) It is assumed that the most complex inactive element has a difference in limit of mass-number of 8 units, has only two odd isotopes, and that the mass-numbers of these are neither the highest nor lowest of all. If all even mass-numbers are included between the limits, the element must have five even and two odd isotopes. Examples of this class are xenon (54) and tin (50). Their odd mass-numbers are numerically second and fourth lowest. This is considered to be typical of the class.
- (b) A less complex class is regarded as obtained from the more complex class by discarding the two lowest isotopes. This class has consequently a difference in limit of mass-number of 6, four possible even isotopes and one odd, which is, in mass-number, second lowest. Mercury (80) with limits of mass-number of 198 and 204 is considered typical of this class.
- (c) The next class, obtained from the one above in the same way as it was obtained, has a difference in mass-number of 4, and in consequence three even isotopes only. Special cases of this class are those with two and with one isotope only.

Even elements in the range  $z=36$  to  $z=82$  have already been divided into classes (2), (3), and (4), mentioned above in the earlier paper. Possibly complex elements without odd isotopes were given in the first column of Table IX.; those with one odd isotope in the second column of the same table, and those with two odd isotopes in the third column.

There are possibly one or more groups in the class without odd isotopes that are simple. The criterion of the simplicity of an element in absence of experimental evidence would be the possession of an atomic weight approximately an integer, and of the form  $4k$ , since all even simple elements according to Aston's work are of this form. In Table I. are arranged the groups of elements without odd isotopes and their atomic weights. It is seen that the only group which appears simple is the group  $16n+10$ , and it will be taken to be so in what follows.

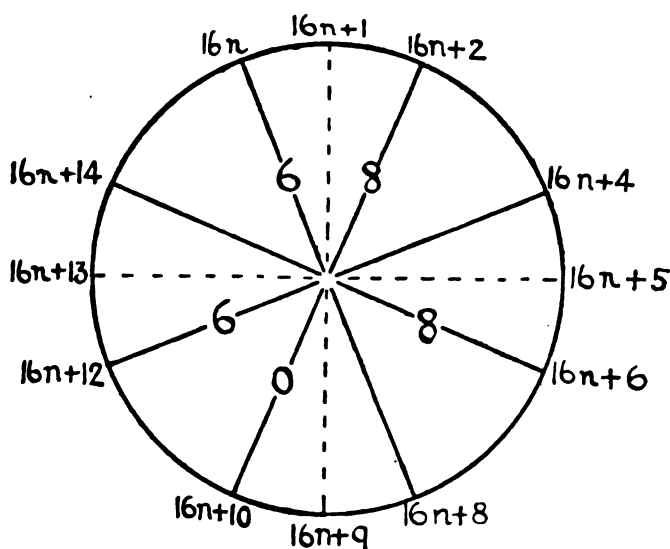
Of the eight groups into which the even elements may be divided in the range under consideration, the groups  $16n$  and  $16n+12$ , having one odd isotope per element, have a range of mass-numbers of 6,  $16n+2$  and  $16n+6$  a range of 8, and the group  $16n+10$  a range of 0, since

TABLE I.

Element.	Atomic weight.	Element.	Atomic weight.
Iron (26) .....	55.85	Zinc (30) .....	65.37
Molybdenum (42) .....	96.0	Palladium (46) .....	106.7
Cerium (58) .....	140.25	Samarium (62) .....	150.4
Tungsten (74) .....	184.0	Platinum (78) .....	195.2
Calcium (20) .....	40.06	Chromium (24) .....	52.0
Krypton (36) .....	82.92	Zirconium (40) .....	90.6
Tellurium (52) .....	127.5	Barium (56).....	137.37
Erbium (68) .....	167.7	Hafnium (72) .....	?

it is likely to be simple. The ranges of the three others may be guessed at by making use of the diagram, fig. 1, which is very similar to fig. 1 of the earlier paper, and

Fig. 1.



illustrates the periodicity of the complexity of even elements in the range considered. The group-numbers  $16n$ ,  $16n + 2$ , etc. are arranged in order round a circle, and the difference in limits of their mass-numbers, where known, placed on their radii. As before, the lines joining  $16n + 1$  and  $16n + 9$  and  $16n + 5$  and  $16n + 13$  are the axes of symmetry. Each known limit on the right of the former

axis of symmetry is 2 greater than its corresponding limit on the left. It would follow, therefore, that the limit for the group  $16n+8$  is 2, and those for groups  $16n+14$  and  $16n+4$ , 0 and 2 respectively, or 2 and 4 respectively. Table II. sets forth these results more explicitly.

TABLE II.

Difference in limits of mass-number.	Atomic number of element.
8 .....	82, 70, 66, 54, 50, 38, 34.
6 .....	80, 76, 64, 60, 48, 44.
4 .....	Possibly 68, 52, 36.
2 .....	72, 56, 40, and possibly 68, 52, 36, 78, 62, 46.
0 .....	74, 58, 42, and possibly 78, 62, 46.

### § 3. *Absolute Values of the Limits of Mass-Numbers of Complex Elements.*

It is, of course, possible that the assumptions which led to the above results are unnecessarily simple. It is interesting, therefore, to see if another line of inquiry will support or modify them. The likeliest method of attack appears to be a consideration of the absolute values of the limits of mass-numbers. These are known for the radio-elements 92, 90, 88, 86, 84, and 82, and for the inactive elements 80, 54, 50, 36, and 34, and will be made use of in this section.

A radioactive isobare is not usually the first or second isotope in importance of an element; it does not belong to more than two elements; and it appears to be connected numerically with the atomic numbers which share it according to a rule analogous to two mentioned in Part I. This is that if  $a_1$  be an even isobare,  $z_1$  and  $z_2$  the atomic numbers of the element sharing the mass-number, and  $\delta$  numerically the difference  $a_1 - (z_1 + z_2)$ , then  $\delta$  applies to one pair of elements only. Table III. A illustrates this. It includes all radioactive isobares of even mass-number.

TABLE III. A.

$\delta$ .	$z_1$ .	$z_2$ .	$a_1$ .	Radioactive products.
52	92	90	234	UX <sub>1</sub> , U <sub>II</sub> .
50	90	88	228	MsTh <sub>1</sub> , Ra.
48	84	82	214	RaC', RaB.
46	84	82	212	ThC', ThB.
44	84	82	210	Po, RaD.

It has been pointed out by W. P. Widdowson and the

writer \* that when an element has an odd isotope the limits of its mass-numbers are usually from 5 above the higher isotope (if there be two) to 1 below the lower. Since all odd isotopes belonging to even elements were deduced in Part I., the limits of all elements with odd isotopes are known if this rule be made use of. The limits of the other elements, however, are not known except those of the class  $16n+10$  which is considered simple. The remaining limits may be obtained, however, if the isobare rule mentioned above be applied to inactive elements.

The results of doing the latter are included in Table III. B, and from the results of both parts of Table III., Table IV. is compiled.

TABLE III. B.

$\delta$ .	$z_1$ .	$z_2$ .	$a_1$ .	Authority.
42	82	80	204	—
40	78	76	194	—
38	72	70	180	—
36	72	70	178	—
34	68	66	168	—
32	68	66	166	—
30	66	64	160	—
28	62	60	150	—
26	56	54	136	—
24	54	52	130	—
22	54	52	128	—
20	54	52	126	—
18	50	48	116	—
16	46	44	106	—
14	?	?	—	—
12	36	34	82	Aston.
10	36	34	80	Aston.
8	36	34	78	Aston.
8	34	32	74	Aston.
8	32	30	70	Aston.

It is seen in Table III. B that the isobare rule breaks down at the difference 8 which applies to no less than three sets of elements. In this respect it resembles the analogous rules referred to. No elements appear to correspond to the difference 14. If strontium had an isotope of 92, or krypton one of 88, or selenium one of 84, a pair of elements could be found for it; but the first two of these possibilities are unlikely, and there is no experimental evidence for the third. The gap arises owing to the anomalous value of the principal isotope of zirconium.

\* W. P. Widdowson & A. S. Russell, *Phil. Mag.* xlviii. p. 293 (1924).



The expected value, as will be shown in the next section, is 94; the value of the atomic weight suggests strongly 90. If the higher value was the real one, strontium would be a complex element, though less complex than others of the class  $16n + 6$ , and have an isotope 92 isobaric with one belonging to zirconium. But as zirconium's principal isotope is 90, strontium is limited to the isotopes

TABLE IV.

Element.	Limits of Mass-number.
U (92) .....	234-240
Th (90) .....	228-234
Ra (88) .....	224-228
Em (86) .....	220-222
Po (84) .....	210-218
Pb (82) .....	204-214
Hg (80) .....	198-204
Pt (78) .....	194-196
Os (76) .....	188-194 or 186-194
W (74) .....	—
Hf (72) .....	178-180 or 178-182
Yb (70) .....	172-180
Er (68) .....	166-168 or 166-170
Dy (66) .....	160-168
Gd (64) .....	154-160
Sn (62) .....	150-152
Nd (60) .....	144-150 or 142-150
Ce (58) .....	—
Ba (56) .....	136-138
Xe (54) .....	126-136
Te (52) .....	126-130
Sn (50) .....	116-124
Cd (48) .....	110-116
Pd (46) .....	106-108
Ru (44) .....	100-106 or 98-106
Mo (42) .....	—
Zr (40) .....	90-92 or 90-94
Sr (38) .....	—
Kr (36) .....	78-86

88 and 86, since it may not have a mass-number which is the principal mass-number of another element. The isobare rule excludes the second isotope, since the difference 12 is assigned to elements 36 and 34. Strontium\* is consequently a simple element, as Aston finds.

In Table IV. are given some alternative possibilities

\* If it were complex, the probability that its isotopes are 88 and 86 only is much greater than that of another possibility.

consistent with the data of Table III. They occur chiefly with elements in the neighbourhood of simple elements. Comparing the data of Table IV. with the limits assigned to the elements in Table II. the following points arise :—

- (a) Elements 78, 62, and 46 are probably not simple but have two isotopes.
- (b) Elements 72, 56, and 40 have probably each two isotopes only but possibly three.
- (c) Elements 68, 52, and 36 have each probably three isotopes.
- (d) Lead (82) has isotopes from 204–212 considered as a common element, and includes 214 as a radio-element. The mass-number 204 is demanded both by the isobare rule and also by the rule connecting limits with the values of odd isotopes.
- (e) Xenon (54) has also apparently a range of 10, but the value 126 is demanded only by the isobare rule. If this isotope is genuine it is probably a “second-order” isotope for, as will be seen in § 5, it does not fit in with the other even isotopes of this element.
- (f) Mass-numbers 186, 170, 142, 98, and 94 may be missing, but if not they are probably isotopes of minor importance of elements 76, 68, 60, 44, and 40 respectively.

#### § 4. *Order of the Masses of Isotopes.*

Three things at least must be known before the masses of the isotopes of an element may even approximately be arranged in the order of their importance: (1) the chief even isotope, (2) the second even isotope, and (3) the relation between mass-number and stability. The second of these has been the most difficult to discover, and except in very easy cases I have not been able to find out how to calculate it. The third will be discussed in § 5; and the first now.

It is clear from Aston's results that the chief even mass-number of an element cannot be guessed at from the latter's atomic weight; the more complex the element and the closer the masses of isotopes are, the more likely is such a guess to be in error. On the other hand, if an element has two isotopes only the relative importance of each may be easily ascertained.

The chief even isotope of an even element is related in many cases to the isotope or the lower isotope of the element next below it by the empirical rule that it is 5 or 3 units

greater according as the even element is complex or simple. The values of the odd isotopes are those predicted in Part I. Secondly, in many cases the value of the chief isotope ascends by 6 units from one even element to another when the latter is complex, and by 2 units when the latter is simple. Thirdly, in several cases the principal even isotope is three units above the

TABLE V.

Atomic Number.	Calculated Values.			Experimental.	Authority.
	1st Method.	2nd Method.	3rd Method.		
92	236	(238)	238	238	At.-wt.
90	232	232	—	232	At.-wt.
88	—	226	226	226	At.-wt.
86	—	220	222	222	Radioactivity.
84	214	214	—	210	Radioactivity.
82	208	208	208	206 or 208	Radioactivity.
80	200	202	202	202	At.-wt.
78	198	196	—	—	—
79	190	190	192	—	—
47	184	184	—	184	At.-wt.
72	182	182	—	—	—
70	176	176	176	—	—
68	170	170	—	—	—
66	164	164	164	—	—
64	156	158	158	—	—
62	152	152	—	—	—
60	146	146	148	—	—
58	140	140	—	140	At.-wt.
56	138	138	—	—	—
54	132	132	132	132	Aston.
52	126	126	—	128	At.-wt.
50	120	120	120	120	Aston.
48	112	114	114	—	—
46	108	108	—	—	—
44	102	102	104	—	—
42	96	96	—	96	At.-wt.
40	94	94	—	90	At.-wt.
38	88	88	—	88	Aston.
36	84	86	86	84	Aston.
34	80	80	80	80	Aston.
32	74	74	—	72	Aston.
30	68	68	—	64	Aston.
28	64	62	—	58	Aston.
26	60	56	—	56	Aston.

lower of its two odd isotopes when there are two, and three units above its odd isotope when there is one. The chief even isotopes derived in these ways are included in Table V., which contains also such experimental values as are known.

It is seen that the agreements are poor for elements below selenium (34), but that, in the range under consideration, they are, on the whole, good. Alternative experimental values of lead's (82) chief isotope have been given. Radioactivity favours the lower value; the atomic weight determination the higher. It has not yet been done by the positive-rays method. Outstanding discrepancies between the experimental and calculated values are seen in the principal isotopes of zirconium (40) and of polonium (84). In no case in the range considered are there more than two different values for the four results.

I have not been able to estimate by a general method the values of the second even isotopes.

#### § 5. *Stability of the Nucleus a function of the Mass-Numbers of Isotopes.*

There are two relations in radioactivity known as Fajans'  $\alpha$ -ray and  $\beta$ -ray rules which connect the mass-numbers of isotopes with the stability of their nuclei. The  $\alpha$ -ray rule is that  $\alpha$ -ray isotopes of ascending mass-number have periods in ascending magnitude; the  $\beta$ -ray rule that  $\beta$ -ray isotopes of ascending mass-number have periods in descending magnitude. To these empirical rules there are, as is well known, a few exceptions. The  $\alpha$ -ray rule holds perfectly for the isotopes of elements 92, 90, and 86, holds partly for elements 88 and 84, and does not fail completely for any element. The  $\beta$ -ray rule holds perfectly for elements 89, 83, and 81, holds partly for element 82, but fails for element 90. Table VI. contains the data on which these statements are based. In this table it is assumed that actinuranium (AcU) is the head of the uranium series and the parent of uranium Y, the product of which is proto-actinium. This appears to me to be in better accord with present knowledge than the commonly-accepted view. This assumption, however, does not affect the validity of the empirical rules under discussion. The table includes also the assumed isotopes of the inactive elements bismuth and thallium.

TABLE VI.

Element.	Descending order of the periods of isotopes with their radiations and mass-numbers.				
Uranium (92) .....	U <sub>I</sub> , ( $\alpha$ ); 238	AcU, ( $\alpha$ ); 235	U <sub>II</sub> , ( $\alpha$ ). 234		
Protoactinium (91).	Pa, ( $\alpha$ ); 231	UX <sub>2</sub> , ( $\beta$ ); 234	UZ, ( $\beta$ ). 234		
Thorium (90) .....	Th, ( $\alpha$ ); 232	Io, ( $\alpha$ ); 230	RdTh, ( $\alpha$ ); 228	UX <sub>1</sub> , ( $\beta$ ); 234	RdAc, ( $\alpha$ ); 227
Actinium (89) .....	Ac, ( $\beta$ ); 227	MsTh <sub>2</sub> , ( $\beta$ ). 228			UY, ( $\beta$ ). 231
Radium (88).....	Ra, ( $\alpha$ ); 226	MsTh <sub>1</sub> , ( $\beta$ ); 228	AcX, ( $\alpha$ ); 227	ThX, ( $\alpha$ ). 224	
Emanation (86) ...	Rn, ( $\alpha$ ); 222	Tn, ( $\alpha$ ); 220	An, ( $\alpha$ ). 219		
Polonium (84) .....	Po, ( $\alpha$ ); 210	RaA, ( $\alpha$ ); 218	ThA, ( $\alpha$ ); 216	AcA, ( $\alpha$ ); 215	RaC', ( $\alpha$ ); 214
Bismuth (83) .....	Bi; 209	RaE, ( $\beta$ ); 210	ThC, ( $\beta$ ); 212	RaC, ( $\beta$ ); 214	AcC, ( $\alpha$ ). 211
Lead (82).....	RaQ', (206) AcQ', (207); ThQ', (208) RaQ'', (210)	RaD, ( $\beta$ ); 210	ThB, ( $\beta$ ); 212	AcB, ( $\beta$ ); 211	RaB, ( $\beta$ ). 214
Thallium (81) .....	Tl, (203) Tl, (205)	AcC'', ( $\beta$ ); 207	ThC'', ( $\beta$ ); 208	RaC'', ( $\beta$ ). 210	

From the above table, however, two wider generalizations may be deduced and these, it will be shown, apply approximately also to the isotopes of inactive elements to the extent they have so far been experimentally determined. These are:—

- I. In elements of odd atomic number the isotope of lowest mass-number has the largest period.
- II.(a) In elements of even atomic number the order of the periods of even mass-numbers is given by a clockwise arrangement of these mass-numbers. \* Going clockwise round the face gives an “ascending” series, and counter-clockwise a “descending” series.
- (b) In an “ascending” series the odd mass-number is in its order of intensity when placed immediately before the mass-number three units greater.
- (c) In a “descending” series the odd mass-number is in its order of intensity when placed immediately after the mass-number which is one greater when the series descends continuously; and immediately after the highest mass-number when it does not.

It is seen from Table VI. that rule I. holds perfectly for all odd elements included in it. It is immaterial whether the isotope emit any radiation or not, or whether it be of even or of odd mass-number. The application of this rule to inactive elements has already been discussed in Part I. of this paper.

Rule II. is much less definite, and with the meagre data available it is difficult to know what, if any, is its bearing on the question of the stability of the nucleus. It is seen from Table VI., however, that the first part of the rule, II.(a), holds for all elements, for which data are available, except uranium ( $z=92$ ). This element alone contains no product of another element as an isotope, and is consequently in an exceptional position. The rule would require mass-numbers for uranium of 238, 240, 234, and 236, or of 238, 236, 234, and 240 in descending order of period. The experimental evidence neither favours these possibilities nor is against them. It is possible that at a former epoch, or even now, one of them represents uranium  $\dagger$ .

In Table VII. is seen how the rule applies to the isotopes of inactive elements. For these elements "relative concentration" must be substituted for "period." It is seen that the agreement is fair. Points where experimental work and the rule disagree are underlined.

TABLE VII.

Element.	Descending order of importance of masses.	
	Experimental.	According to Rule II.
Mercury (80) .....	202, { <u>200</u> }, 204*	202, 200, 198, 204
Xenon (54) .....	132, 134, 136, 128, 130, <u>126, 124</u>	132, 134, 136, 128, 130
Tin (50) .....	120, 118, 116, 124, 122	120, 118, 116, 124, 122
Krypton (36) .....	<u>84, 86, 82</u> , 80, 78	<u>86, 84, 82</u> , 80, 78
Selenium (34) .....	80, 78, 76, <u>82, 74</u>	80, 78, 76, 82
Calcium (20) .....	40, 44	40, 44, <u>42</u>
Argon (18) .....	40, 36	40, 36, <u>38</u>

\* This arrangement is most consistent with Aston's results and with the accepted atomic weight.

$\dagger$  See also G. Kirsch, *Sitzb. Akad. Wiss. Wien*, vol. cxxxi. p. 551 (1922).

The rule does not give the minor isotopes of xenon or that of selenium. These lie outside the limits of mass-number for which it is operative, because from the number and value of the odd isotopes of these elements the limits of xenon are regarded as 128-136 and of selenium 76-82.

The exact relation of the relative concentrations of odd to those of even isotopes in an element of even atomic number is a more difficult problem. In "ascending series" like that of lead (82) (Table VI.) or of xenon (54) (Table VII.), odd isotopes are among the principal ones, and their position is given by rule II.(b) above. According to Fajans'  $\beta$ -ray rule an "ascending series" is a series of isotopes all of which expel  $\beta$ -particles, but the order of the isotopes of lead, the only even element that possesses such a series, is given better by rule II. than by the  $\beta$ -ray rule.

Most series, however, are "descending" series like those of thorium (90), mercury (80), and tin (50), and in these the odd isotope is of less importance and in some cases of minor importance Fajans'  $\alpha$ -ray rule would demand that it be placed next below the mass-number one unit greater if the latter were an  $\alpha$ -ray body. This rule generalized to exclude the provisos of radioactivity holds (see Table VI.) for the positions of radioactinium (88), acton (86), actinium A (84), and for actinuranium (92) if uranium's second isotope has a mass-number 236. It would hold also for radioactinium (90) if the period of this body were greater than that of uranium X. (The periods are close, however, 19.5 days and 24.6 days respectively.) It fails to account for the position of uranium Y as does Fajans'  $\beta$ -ray rule also. Among the inactive elements it may apply to mercury's isotope of 199, but it does not apply to the odd isotopes of tin (50), krypton (36), or selenium (34). Rule II.(c), on the other hand, applies to the odd isotopes of uranium, thorium, radium, emanation, polonium, lead, tin, and selenium, might apply to that of mercury, and fails only for the isotope 83 of krypton. The experimental data in support of this are given in Table VI. above and in Table VIII. below.

TABLE VIII.

Element.	Descending order of intensities of isotopes.
	200 202, 199? } 198 }
Mercury (80) .....	202, 199? , 204, 199?
Tin (50) .....	120, 118, 116, 124, 119, 117, 122
Krypton (36) .....	84, 86, 82, 83, 80, 78
Selenium (34).....	80, 78, 76, 82, 77, 74

§ 6. *The Order of the Masses of Isotopes.*

The lack of knowledge regarding the second even isotope of an even element prevents a prediction of the order of the masses of isotopes for the complex elements, even when their number and absolute values have been estimated. This would not matter if one knew when a series of isotopes was an "ascending" or a "descending" one, but this is evidently not a periodic property since lead (82) has an "ascending" series and tin (50) a "descending" one. If dysprosium (66) has the former its order would be according to Tables IV., V., and rule II., 161, 164, 163, 166, 168, 160, 162; if the latter, 164, 162, 160, 168, 163, 161, 166. The atomic weight, 162.5, is consistent with either.

If ytterbium (70) has a series similar to xenon (54) its order would be similarly 173, 176, 175, 178, 180, 172, 174, and, if it has a "descending" series, it would be 176, 174, 172, 180, 175, 173, 178. The atomic weight, 173.5, is in favour of the former, but this may not be a very exact value. Cadmium (48) if "descending" should have 114, 112, 110, 116, 111, or 112, 110, 116, 114, 111 according as 114 or 112 is the principal even isotope, and, if "ascending," 111, 114, 116, 110, 112, or 112, 111, 114, 116, 110. The first and fourth of these are most probable, since neither 112 nor 114 is likely to be of minor importance. The atomic weight, 112.41, is not decisive but favours the first and third; analogy with mercury (80) favours the first.

Others may be worked out in this way, but obviously an ambiguous answer may be given even when the principles laid down here are kept strictly. The evidence of atomic-weight favours "ascending" series for ruthenium (44) and for neodymium (60), the former commencing on the mass-number 100, the latter on 144; it favours also "descending" series for osmium (76) and for gadolinium (64), the former commencing on the mass-number 192, the latter on 158. The elements without odd isotopes appear easier: platinum (78) is likely to have isotopes of 196 and 194 only; hafnium (72) 180 and either or both of 182 and 178; erbium (78) 170, 168, 166; samarium (62) 152 and 150; barium (56) 138 and 136; tellurium (52) 126, 128, 130; palladium (46) 106 and 108, and zirconium (40) 90 and 92. Tungsten (74), cerium (58), molybdenum (42), and probably strontium are simple.



*Summary.*

(1) The complexity of the elements of even atomic number between selenium and lead is investigated on the lines employed in Part I.

(2) The number of isotopes and their mass-numbers are calculated for each element in the range investigated on the assumption that the complexity of the elements is a function of the atomic number 16 and by making use of empirical relations that apply equally to radioactive isotopes and to those of ordinary elements.

(3) A generalization similar to, but wider than Fajans'  $\alpha$ - and  $\beta$ -ray rules for the order of the masses of isotopes is stated, and is found applicable both to radioactive isotopes and to those of ordinary elements so far experimentally investigated.

(4) With the help of this generalization an attempt is made to predict the order of the masses of isotopes of many elements still to be examined by the positive-ray method.

Dr. Lee's Laboratory,  
Christ Church, Oxford.  
May 1923.

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*XL. The Selection Principle: A Development based upon the Stokes-Thomson Pulse Theory. By C. N. WALL\*.*

**T**HE selection principle which states that the azimuthal quantum number can change at most by unity in any interorbital transition of an electron is due to Rubinowicz\*. Bohr† has also deduced a restricted selection principle which excludes a zero change in angular momentum. A rigorous development of this principle demands extensive knowledge of the classical electrodynamics and vector analysis. However, this principle may be deduced very simply though with less rigour by basing the deduction upon the Stokes-Thomson pulse theory for an electron and certain ramifications of this theory.

Consider the changes which take place, according to the quantum theory of electronic orbits, when an electron such

\* Communicated by Prof. Jakob Kunz.

† Rubinowicz, *Phys. Zeit.* xix, pp. 441 and 465 (1918); Sommerfeld, *Atombau*, 3d Ed., pp. 310-339 and Appendix.

† Bohr, "Quantum Theory of Line Spectra," Pts. I. and II., Danish Academy of Science.

as in an ion of helium undergoes an interorbital transition and radiates light. In such a transition the electron loses a certain amount of energy, namely,  $\Delta E = E_1 - E_2$ , where  $E_1$  represents the total energy of the electron in its initial orbit and  $E_2$  the total energy in its final orbit. This loss of energy is radiated in the form of electromagnetic waves whose frequency  $\nu$  is given by the relation

$$\Delta E = h\nu,$$

where  $h$  is Planck's constant. In addition to the loss in energy the electron suffers a certain change in angular momentum,  $\Delta P = |P_1 - P_2|$ , where  $P_1$  and  $P_2$  designate respectively the angular momentum of the electron in its initial and final orbit. It is assumed that this change in angular momentum suffered by the electron in its transition is carried away by its radiation, so that both energy and angular momentum are conserved. In other words, the radiation emitted by the electron in its interorbital transition contains within itself both the energy and the angular momentum given up by the electron in its transition. The plausibility of such an assumption as the conservation of angular momentum is greatly strengthened if one remembers that circularly polarized light should contain both energy and angular momentum\*.

It is necessary to determine the relation between  $\Delta E$  and  $\Delta P$ . In order to do this we make use of the classical theory of electrodynamics and work with what may be termed the equivalent path of an electron in the classical theory, or what is sometimes referred to as a vibration ellipse of an electron. In short, we make the assumption that an electron jumping from an initial orbit to a final orbit according to the quantum theory is in a sense equivalent in classical electrodynamics to an electron undergoing simple harmonic motion of frequency  $\nu$  along two perpendicular axes  $X$  and  $Y$  with amplitudes  $a$  and  $b$  respectively and a phase difference of  $\pm \frac{\pi}{2}$ .

Thus the vibration electron has an ellipse as its orbit with semi-axes  $a$  and  $b$ . The coordinates of this vibration or equivalent electron in its vibration or equivalent path at any instant  $t$  are evidently

$$\left. \begin{aligned} x &= a \cos 2\pi\nu t \\ y &= b \sin 2\pi\nu t. \end{aligned} \right\} \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (1)$$

\* Poynting, 'Collected Scientific Papers,' pp. 372-379.

Its velocity components are

$$\left. \begin{aligned} x' &= \frac{dx}{dt} = -a2\pi\nu \sin 2\pi\nu t, \\ y' &= \frac{dy}{dt} = b2\pi\nu \cos 2\pi\nu t. \end{aligned} \right\} \dots \dots (2)$$

The acceleration components are

$$\left. \begin{aligned} x'' &= \frac{d^2x}{dt^2} = -a(2\pi\nu)^2 \cos 2\pi\nu t, \\ y'' &= \frac{d^2y}{dt^2} = -b(2\pi\nu)^2 \sin 2\pi\nu t. \end{aligned} \right\} \dots \dots (3)$$

As this so-called vibration electron moves around its elliptical orbit it radiates both energy and angular momentum according to the classical theory. Furthermore, by hypothesis the relation between this radiated energy and angular momentum is identical with the relation between  $\Delta E$  and  $\Delta P$ . Thus it is only necessary to determine the relation between the energy and the angular momentum radiated by a vibration electron in one or more complete vibrations.

Sir G. Stokes first suggested that an electron suffering an impulse would send out an electromagnetic pulse emitted at the instant of the impulse. Sir J. J. Thomson \* calculated the energy radiated by such an electron, and Larmor extended the theory to the case of an accelerated electron. It may easily be shown † by this theory that the rate of radiation of energy from an electron accelerated along the X-axis is given by

$$\left( \frac{dE}{dt} \right)_x = \frac{2e^2}{3c} x''^2, \dots \dots \dots (4)$$

where  $e$  represents the electronic charge,  $c$  the velocity of light, and  $x''^2$  the square of the acceleration of the electron along the X-axis. A similar equation may be written for acceleration along the Y-axis. A more rigorous analysis ‡ of the problem leads to the conclusion that expression (4) is not accurate if one desires to compute the rate of radiation of energy from an accelerated electron at any special instant. However, the total emission of radiation through a sufficiently

\* J. J. Thomson, *Phil. Mag.* xlv. p. 172 (1898).

† J. A. Crowther, 'Ions, Electrons, and Ionizing Radiations,' pp. 143-147.

‡ Jeans, 'Electricity and Magnetism.' Sec. 649, 4th Ed.

large interval of time is accurately given upon integrating the expression through this time interval. Fortunately it is in this sense that we are going to use the expression.

Suppose now that we look upon this radiation by an accelerated electron as implying the existence of a reactive force acting upon the electron. If  $F_x$  and  $F_y$  represent the components of this reactive force due to radiation then obviously the following equations must hold,

$$\left. \begin{aligned} F_x x' &= \frac{2e^2}{3c} x'^2, \\ F_y y' &= \frac{2e^2}{3c} y'^2. \end{aligned} \right\} \dots \dots \dots (5)$$

By means of these equations it is possible to calculate the values of  $F_x$  and  $F_y$ . It must not be inferred, however, that the above values of  $F_x$  and  $F_y$  represent the total reactive forces acting upon the electron.  $F_x$  and  $F_y$  are only the non-conservative forces acting upon the electron due to the friction-like effect of energy radiation. There are certain conservative forces which also act upon the electron. If all these forces are taken into consideration then it has been shown by Lorentz\* that the total reactive force upon the electron should be directly proportional to the first derivative of the acceleration of the electron. Nevertheless, in determining the value of the energy and the angular momentum radiated by the vibration electron in any integral number of whole vibrations a time integral around the entire ellipse is required, so that the energy and angular momentum contributed by the conservative reactive forces acting upon the electron vanish for such an integration and the non-conservative reactive forces alone furnish the value of the integral. Accordingly the same result is obtained if one uses the total reactive force on the electron.

The next task is to set up expressions for both the energy and the angular momentum radiated by the vibration electron during any integral number of complete vibrations. Evidently the total energy radiated during  $n$  (positive integral number) complete vibrations is given by the expression

$$E_n = \int_0^n (x' F_x + y' F_y) dt. \dots \dots (6)$$

\* Lorentz, 'The Theory of Electrons,' p. 251.

The total angular momentum radiated for  $n$  complete vibrations is given by the expression

$$P_n = \int_0^n (xF_y - yF_x) dt. \quad . \quad . \quad . \quad (7)$$

Let us multiply equation (6) through by the constant  $k = \frac{2ab}{a^2 + b^2} \frac{1}{2\pi\nu}$  and subtract the resulting form from equation (7). We have

$$\left. \begin{aligned} P_n - kE_n &= \int_0^n \left[ (xF_y - yF_x) - k(x'F_x + y'F_y) \right] dt \\ &= \int_0^n \left[ F_x(-kx' - y) + F_y(-ky' + x) \right] dt. \end{aligned} \right\} \quad (8)$$

If now we substitute in the right-hand member of expression (8) the values of  $F_x$  and  $F_y$  as determined in equations (5), and then make the further substitutions for  $x, y, x', y', x''$ , and  $y''$ , as determined in equations (1), (2), and (3), the integrand simplifies considerably. Upon carrying out the indicated integration the right-hand member vanishes for all positive integral values of  $n$ . Thus we obtain the relation

$$P_n = kE_n = \frac{E_n}{2\pi\nu} \frac{2ab}{a^2 + b^2}, \quad . \quad . \quad . \quad (9)$$

which gives the relation between the energy and angular momentum radiated by the vibration electron in  $n$  complete vibrations.

By taking the finite differences of  $P_n$  and  $E_n$  with respect to  $n$  we get at once

$$\Delta P = \frac{\Delta E}{2\pi\nu} \frac{2ab}{a^2 + b^2}. \quad . \quad . \quad . \quad (10)$$

In accordance with our assumptions this relation deduced by classical methods is the relation between the change in energy and angular momentum of an electron undergoing an interorbital transition. But for such a transition

$$\Delta P = |P_1 - P_2| = \frac{h}{2\pi} |m_1 - m_2|,$$

since

$$P_1 = \frac{m_1 h}{2\pi} \quad \text{and} \quad P_2 = \frac{m_2 h}{2\pi},$$

$m_1$  and  $m_2$  being respectively the azimuthal quantum numbers for the initial and final orbits. Also  $\Delta E = h\nu$ .

Therefore expression (10) becomes after these substitutions

$$|m_1 - m_2| = \frac{2ab}{a^2 + b^2}. \quad (11)$$

In short, we arrive at expression (11) by quantizing the classical relation (10).

Now

$$2ab \leq a^2 + b^2 \quad \text{since} \quad (a - b)^2 \geq 0.$$

Therefore

$$|m_1 - m_2| \leq 1.$$

Since by the quantum theory  $m_1$  and  $m_2$  must be positive integers it follows that the difference between  $m_1$  and  $m_2$  can only be  $\pm 1$  or zero, *i.e.* we have the three cases

$$\left. \begin{aligned} m_1 - m_2 &= +1, & a = b & \text{since} & \frac{2ab}{a^2 + b^2} &= 1, \\ m_1 - m_2 &= -1, & a = b & \text{since} & \frac{2ab}{a^2 + b^2} &= 1, \\ m_1 - m_2 &= 0, & a = 0, b = 0, & \text{or} & a = b = 0. \end{aligned} \right\} (12)$$

The relations (12) give at once the essence of the principle of selection: the azimuthal quantum number can change at most by unity in any interorbital transition of the electron. The polarization rule follows immediately: if the azimuthal quantum number changes by  $\pm 1$  the light emitted because of an interorbital transition will be circularly polarized; otherwise, there will be linear polarization.

In conclusion it might be well to point out that the development of the selection principle depends upon the quantizing of a relation developed by the use of classical electrodynamics. It states that only those interorbital transitions are possible in the quantum theory in which the accompanying changes of energy and angular momentum are compatible with the classical theory. In this sense the principle of selection serves as a bond which tends to tie together more closely the quantum theory and the classical theory.

Thanks are due to Professor Jakob Kunz for valuable suggestions in the preparation of this paper.

Laboratory of Physics,  
University of Illinois,  
Urbana, Illinois,  
November, 1923.

XLI. *Quantum Defect and Atomic Number.* By LOUIS A. TURNER, M.A., Ph.D., *Charlotte Elizabeth Procter Fellow in Physics, Princeton University* \*.

THE values of the terms of a series of spectroscopic terms are given by the expression

$$\frac{N}{\{m+a+f(m)\}^2},$$

where  $N$  is the Rydberg constant,  $m$  has different integral values for the different terms with a value of 1 for the first,  $a$  is a constant, and  $f(m)$  is a function of  $m$ , of which the numerical value is small compared with  $a$  and decreases rapidly with increasing  $m$ . For the hydrogen spectrum  $a=0$ ,  $f(m)=0$ , and the values of  $m$  are, according to Bohr's theory, the principal quantum numbers of the corresponding electron orbits. By analogy, the denominator of the more general expression for a term is called the effective quantum number of the term. If  $n$  be the actual principal quantum number of the orbit corresponding to the term, and  $m+a+f(m)$  the effective quantum number, the difference  $q=n-\{m+a+f(m)\}$  is called the quantum defect. As  $n$  is taken larger and larger  $m$  increases by the same amount, but  $f(m)$  diminishes rapidly so that  $q$  approaches a limiting value  $n-m-a$  which equals some small integer minus  $a$ .

The order of magnitude of  $q$  depends upon which of the two possible types of orbit the one in question belongs to. Bohr † calls them orbits of the first kind and orbits of the second kind. Orbits of the first kind are those in which the valence electron remains throughout the orbit completely outside of the region traversed by the inner electrons of the atomic structure. I have discussed elsewhere ‡ a possible interpretation of the difference between the values of the terms corresponding to such orbits for the alkali metal atoms and the ionized atoms having a structure similar to that of Na. The  $q$  values for such orbits are small fractions. Orbits of the second kind are those in which the electron penetrates the region

\* Communicated by Prof. K. T. Compton.

† N. Bohr, *Annalen der Physik*, lxxi. p. 228 (1923).

‡ Louis A. Turner, *Astrophys. Journ.* lviii. 3. p. 176 (1923), and lix. 4. p. - (1924).

traversed by the other electrons and passes close to the nucleus during part of the orbit. For such orbits  $q$  may have a value of several units. For an electron of given energy and angular momentum the contribution to the integral  $\oint p_r dr$ , which gives the radial quantum number,

will be much greater during that part of the orbit when it is close to a nucleus of several units positive charge than it would be for that same part of the orbit in a coulomb field of a single positive charge. The effective or apparent quantum number will therefore be less than the actual one.

If this theory be correct, we should expect that the limiting value of the quantum defect for series of the same type should be a function of the nuclear charge—i. e., of the atomic number. The purpose of the present paper is to point out certain empirical relations of this kind and their bearing upon the theory of atomic structure. The values of the constant  $a$  have for the most part been taken directly from the series formulas or calculated from the term values given in Professor Fowler's Report on Series in Line Spectra. In addition, constants calculated by Fowler\*, Fues†, and Datta‡, and data for Sr given by Saunders§ and for Al<sup>+</sup> given by Paschen ||, have been used. It should be pointed out that  $a$  takes practically the same value, no matter what form of  $f(n)$  is used in the computation. The data for the different types of spectra are presented and discussed separately, and followed by a more general discussion.

### *Doublet Spectra of the Alkali Metal Type.*

Table I. gives the values of the constant  $a$  for the series of the second kind in the spectra of the alkali metal type. The quantum numbers given are those of the largest term of the series, first, as given by Bohr¶ in his theory of atomic structure, and second, as the following work seems to indicate that they should be. There are two corresponding values of the quantum defect.

\* A. Fowler, Proc. Roy. Soc. A, ciii. p. 413 (1923).

† E. Fues, *Ann. d. Phys.* lxiii. p. 21 (1920).

‡ S. Datta, Proc. Roy. Soc. A, xcix. p. 71 (1921).

§ F. A. Saunders, *Astrophys. Journ.* lvi. p. 73 (1922).

|| F. Paschen, *Ann. d. Phys.* lxxi. p. 537 (1923).

¶ N. Bohr, *loc. cit.*



TABLE I.—Doublet Spectra.

Element.	Atomic Number.	Series.	Quantum Numbers (Bohr).		Quantum Numbers (L.A.T.).		$q_s - q_p$ .
			$a$ .	$q$ .		$q$ .	
Li .....	3	$s$	0.60	2 <sub>1</sub>	0.40	2 <sub>1</sub>	0.40
		$p_1$	0.951	2 <sub>2</sub>	0.049	2 <sub>2</sub>	0.049
Na .....	11	$s$	0.650	3 <sub>1</sub>	1.350	3 <sub>1</sub>	1.350
		$p_1$	1.148	3 <sub>2</sub>	0.852	3 <sub>2</sub>	0.852
K .....	19	$s$	0.822	4 <sub>1</sub>	2.178	4 <sub>1</sub>	2.178
		$p_1$	1.296	4 <sub>2</sub>	1.704	4 <sub>2</sub>	1.704
Rb .....	37	$s$	0.87	5 <sub>1</sub>	3.13	6 <sub>1</sub>	4.13
		$p_1$	1.366	5 <sub>2</sub>	2.634	6 <sub>2</sub>	3.634
Cs .....	55	$s$	0.95	6 <sub>1</sub>	4.05	8 <sub>1</sub>	6.05
		$p_1$	1.449	6 <sub>2</sub>	3.551	8 <sub>2</sub>	5.551
Cu .....	29	$s$	0.42	4 <sub>1</sub>	2.58	5 <sub>1</sub>	3.58
Ag .....	47	$s$	0.49	5 <sub>1</sub>	3.51	7 <sub>1</sub>	5.51
Mg <sup>+</sup> .....	12	$s$	0.934	3 <sub>1</sub>	1.066	3 <sub>1</sub>	1.066
		$p$	1.305	3 <sub>2</sub>	0.695	3 <sub>2</sub>	0.695
Ca <sup>+</sup> .....	20	$s$	1.201	4 <sub>1</sub>	1.799	4 <sub>1</sub>	1.799
		$d''$	1.36	4 <sub>3</sub>	1.64	4 <sub>3</sub>	1.64
Sr <sup>+</sup> .....	38	$s$	1.315	5 <sub>1</sub>	2.685	6 <sub>1</sub>	3.685
		$d''$	1.52	5 <sub>3</sub>	2.48	6 <sub>3</sub>	3.48
Ba <sup>+</sup> .....	56	$s$	1.430	6 <sub>1</sub>	3.570	8 <sub>1</sub>	5.570
		$d''$	1.58	6 <sub>3</sub>	3.42	8 <sub>3</sub>	5.42
Ra <sup>+</sup> .....	88	$s$	1.33	7 <sub>1</sub>	4.69	11 <sub>1</sub>	8.69
Zn <sup>+</sup> .....	30	$s$	0.35	4 <sub>1</sub>	2.65	5 <sub>1</sub>	3.65
Cd <sup>+</sup> .....	48	$s$	0.45	5 <sub>1</sub>	3.55	7 <sub>1</sub>	5.55
Al <sup>++</sup> ...	13	$s$	1.10	3 <sub>1</sub>	0.90	3 <sub>1</sub>	0.90
		$p_1$	1.40	3 <sub>2</sub>	0.60	3 <sub>2</sub>	0.60
Si <sup>+++</sup> ...	14	$s$	1.228	3 <sub>1</sub>	0.772	3 <sub>1</sub>	0.772
		$p_1$	1.492	3 <sub>2</sub>	0.508	3 <sub>2</sub>	0.508

Fig. 1 shows the values of  $q$  for series in the neutral atoms plotted against the atomic numbers. If the values of  $q$  for the  $p_1$  series of the alkali metal atoms obtained by the use of Bohr's quantum numbers be plotted, they lie along a broken line ABC, which changes slope at the K point. If, however, the value of  $q$  for Rb be increased by 1, and that for Cs by 2, the straight line ABD passes through the upper four points, the Li point falling slightly above the line. This would seem to indicate that the largest  $p_1$  term of Rb has the quantum numbers 6<sub>2</sub> instead of 5<sub>2</sub> as given by Bohr, and that the largest  $p$  term of Cs has the quantum numbers 8<sub>2</sub> instead of 6<sub>2</sub>.

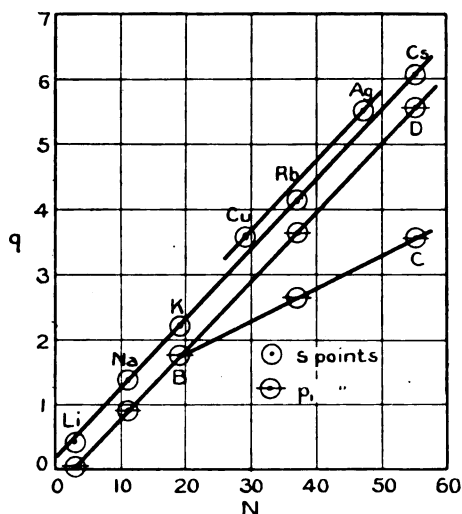
The reasons which make me believe that the present data call for this change are:—

1. If the general theory which accounts for the quantum defect of such orbits is correct, a continuous change with

increasing atomic number would be expected. That it should be a linear relation is surprising, but some sort of a smooth curve would be expected.

2. If a break of the line exists, because of the change of structure occurring in the long periods of the periodic arrangement of the elements, one would not expect the break to occur at the K point. This point would belong to one or the other segment of the line, but not to both, for the K atom must have one or the other structure, and not both.

Fig. 1.



3. It would be a remarkable coincidence if the change of slope were a real one, and yet such that the second line could be swung into the first by this precise integral change in the ordinates of the two points.

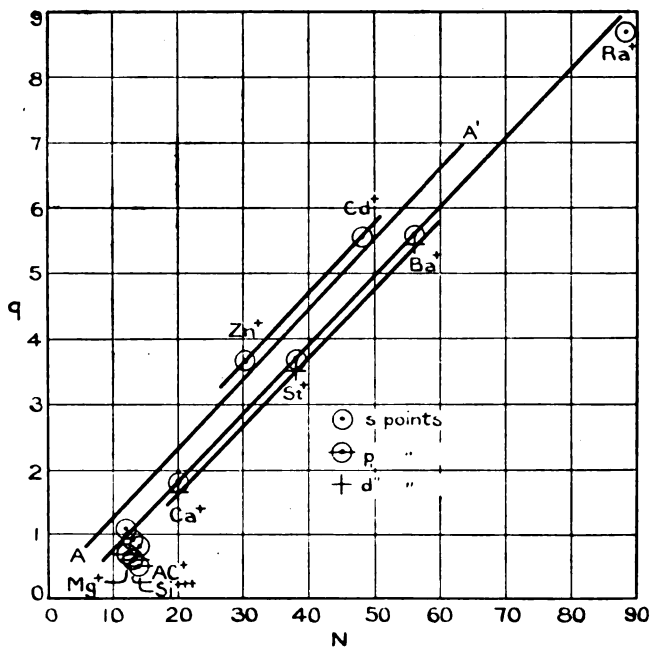
4. The same change produces the same result with other series, as will appear in the sequel.

The corresponding changes have been made in the quantum numbers from which the  $q$ 's for the  $s$  terms of the alkalis have been calculated. Quantum numbers have been assigned to the Cu and Ag terms so as to bring the two points as close to the  $s$  curve for the alkalis as possible. They are 5 and 7 respectively, the two numbers fitting in between the value of 4 for K, 6 for Rb, and 8 for Cs. The equation of the  $p_1$  line is  $q = 0.1068N - 0.322$ . The slopes of the other two lines are

approximately the same. The  $p_1$  line for the alkalis lies a distance of 0.50 below the  $s$  line, as is apparent from the values of  $q_s - q_p$ . The two Li points do not fall very exactly on the lines. This is in agreement with Bohr's statement that the degree of penetration is different for Li.

The  $n$ th  $s$  or  $p_1$  term in the spectrum of an alkali metal is less than the corresponding term in the spectrum of one of lower atomic number. A  $d$  or  $f$  term is larger, however. Hence quantum defects calculated for the  $d$  and  $f$  series could not fit into this scheme, for they do not increase the same way.

Fig. 2.



The orbits corresponding to these terms are apparently orbits of the first kind with quantum numbers as given by Bohr.

On fig. 2 are plotted the data for the spectra of this type given by ionized elements. The quantum numbers used correspond to those used for the data of fig. 1. The line  $AA'$  is the  $s$  line of fig. 1 drawn in so that the two figures can be compared. The orbits for the  $d$  terms are apparently orbits of the second kind for elements of atomic number

higher than that of Ca. The  $Ra^+$  point is not accurately determined because of the lack of sufficient data, but the deviation from the line is probably more than can be accounted for by this error. The  $Zn^+$  and  $Cd^+$  points show a considerable deviation from the alkaline earth metal line, but lie on a line nearly parallel to the others. The points corresponding to ionized elements lie below the lines for the neutral elements of the same spectroscopic type, the distance below being greater the greater the degree of ionization. The  $q_s - q_p$  separation becomes less the greater the degree of ionization.

### Triplet Spectra.

Table II. gives the available data for the triplet spectra of the divalent metals and also of O, S, and Se. Fig. 3 shows

TABLE II.—Triplets.

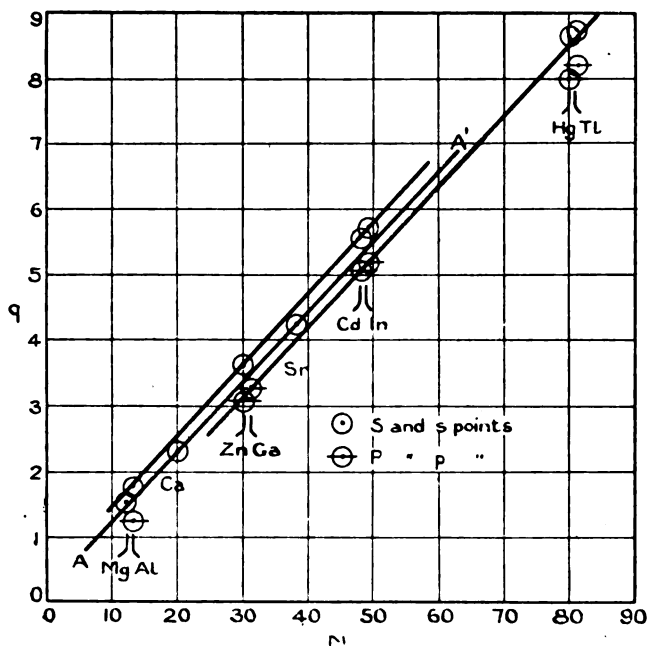
Element.	Atomic Number.	Series.	$\alpha$ .	Quantum Numbers.	$q$ .	$q_s - q_p$
Mg .....	12	$s$	1.377	$4_1$	1.623	
Ca .....	20	$s$	1.561	$5_1$	2.439	
Sr .....	38	$s$	1.631	$7_1$	4.369	
Ba .....	56	$s$	1.73	$9_1$	6.27	
Zn .....	30	$s$	1.28	$6_1$	3.72	0.52
		$p_1$	0.80	$5_2$	3.20	
Cd .....	48	$s$	1.33	$8_1$	5.67	0.53
		$p_1$	0.86	$7_2$	5.14	
Hg .....	80	$s$	1.29	$11_1$	8.71	0.59
		$p_1$	0.88	$10_2$	8.12	
O .....	8	$s$	0.77	$3_1$	1.23	
S .....	16	$s$	0.93	$4_1$	2.07	
Se .....	34	$s$	0.96	$6_1$	4.04	
$Al^+$ .....	13	$s$	0.73	$3_1$	1.27	0.38
		$p$	1.11	$3_2$	0.89	

the lines obtained by plotting these data. The line  $AA'$  is again the  $s$  line from fig. 1. It should be noted that the three  $s$  lines of fig. 3 for the different groups of elements all come very close to that of the alkali metals. The Hg point does not fall on any of these lines, but comes very close with the quantum number taken as indicated. The  $q_s - q_a$  separations for Zn and Cd are 0.52 and 0.53, in fair agreement with the value of 0.50 for the alkalis. This value of 0.52 might be used to predict the wave-numbers of some of the higher  $p$  terms of the spectra of the alkaline earth metals.



data are plotted in fig. 4. Again the S line comes very close

Fig. 4.



to that for the alkali metals (AA'), the P line falls a distance of about 0.55 below it, and the Hg points are too low.

### Doublet Spectra, Al type.

Table IV. gives the data for these series. They are plotted

TABLE IV.

Metal.	Atomic Number.	Series.	$\alpha$ .	Quantum Numbers.	$q$ .	$q_s - q_p$ .
Al .....	13	$s$	1.22	$4_1$	1.78	0.53
		$p_1$	0.75	$3_2$	1.25	
Ga .....	31	$s$	—	—	—	—
		$p_1$	0.72	$5_2$	3.28	
In .....	49	$s$	1.27	$8_1$	5.73	0.53
		$p_1$	0.80	$7_2$	5.20	
Tl .....	81	$s$	1.25	$11_1$	8.75	0.58
		$p_1$	0.83	$10_2$	8.17	

in fig. 4 also. Again the S line comes very close to all the others. The  $q_s - q_p$  differences are again 0.53 for Al and In,

but the difference for Tl is 0.58, and the Tl point falls below the line. The difference for  $Al^+$  is 0.38.

### DISCUSSION.

Apparently any orbit of the second kind can be arbitrarily divided into three parts—one, where it is completely outside of the region of the other electrons and in a field very nearly the same as that of a single positive charge; another, where it is close to the nucleus in a much stronger field; and the third transition part of the orbit when it is passing from one to the other. During this transition the particular structure of the atom will have its greatest effect. The fact that these S lines for the different elements and their different spectral types come so close together, seems to show that this quantum defect depends primarily upon the nuclear charge, and only to a slight extent upon the distribution of electrons in the outer parts of the atom—that is, the general course of the lines depends upon some very fundamental general relation of the electron to the nucleus, but their positions are shifted somewhat for the different outer electron structures. This point of view is in agreement with the changes in the quantum defect for the larger terms corresponding to smaller orbits. For these orbits the influence of the particular structure is of greater influence. This is specially true for the divalent atoms, where the second valence electron is presumably relatively loosely attached, and for which the terms show the greatest deviations from any of the simple series formulas.

The chief problem presented by these relations is the explanation of the linear relationships and the slope of the lines. That I have not been able to solve. The quantum defect for a given orbit is the excess of the contribution to the integral  $\oint p_r dr$  which is made as the electron passes close to the nucleus over what it would have been had the electron remained in the field of a positive charge at a point. The decrease in quantum defect for ionized atom terms would be expected, because this contribution to the integral which must be subtracted is greater the greater the value of the net charge. The problem of calculating how much of a complete orbit the electron traverses in the region of the nucleus, and the contribution to the integral, is a very complicated one, even on the basis of the simplest reasonable assumptions.

If these relationships mean anything at all, we have to face

the alternative of either explaining the sharp break in the curve for quantum defect as a function of atomic number of all of these groups of similar spectra, or of altering the theory of atomic structure in its explanation of the details of the building-up of the atoms through the long periods. For the reasons given above, I think that the latter is necessary. The kernel of Rb will have to contain some orbits of principal quantum number 5 and that of Cs some of numbers 6 and 7. More spectroscopic information must be had before the details of the process can be worked out.

Regardless of the theoretical explanations, these relations should prove useful in working out series in the spectra of the elements ionized to different degrees. The same linear relationships will hold presumably, for they do so for the ionized alkaline-earth series. The parallelism of these lines brings out the fact that the difference between the constants  $a$  for two different series of terms is nearly constant for all elements of the same chemical sub-group. In particular, the difference of 0.50 to 0.55 between  $q_s$  and  $q_p$  for these neutral atoms of different spectroscopic type is worthy of note. I have never seen that fact explicitly pointed out, although it may have had something to do with the use of the values 1.5, 2.5, etc. for  $m$  in the formulas for the  $s$  series. This difference  $q_s - q_p$  is, of course, equal to  $a_p - a_s$ . Perhaps the values for this difference of 0.37, 0.30, and 0.26 as obtained from the  $Mg^+$ ,  $Al^{++}$ , and  $Si^{+++}$  spectra will be common to the spectra of various elements corresponding to these successive stages of ionization. The value of 0.38 for the  $Al^+$  spectra lends support to that expectation. The fact that the four numbers 0.52, 0.37, 0.30, and 0.26 are in the ratio  $1 : 2^{-\frac{1}{2}} : 3^{-\frac{1}{2}} : 4^{-\frac{1}{2}}$  may be of significance.

Mention should be made of the work of Brackett and Birge \*, who discovered similar relationships. They plotted values of the effective quantum number of the various spectroscopic terms as a function of the number of electron groups beneath the valence electron as given by Bohr's theory. Lines were drawn through the points having the same quantum number according to that theory. They also found that corresponding parts of these curves had the same slope, especially for the terms of higher quantum number, and that there were certain recurring differences in these effective quantum numbers for different elements of different groups related similarly in the periodic arrangement. The present arrangement gives these results, and, in addition, gives a

\* F. S. Brackett and R. T. Birge, Jour. Op. Soc. Am. viii, p. 213 (1924).



better correlation of elements of the same chemical group, and brings out more clearly the fundamental regularities common to all.

#### SUMMARY.

1. It is found that by increasing Bohr's quantum numbers for the valence electrons of elements of atomic number greater than 28, limiting quantum defects can be computed which are linear functions of the atomic number, for corresponding series, for elements of the same chemical sub-group.

2. The slopes of these lines are all very nearly the same.

3. The *s* lines for elements of different chemical nature come very close together, indicating that the quantum defect depends primarily upon the atomic number and secondarily upon the particular atomic structure.

4. The *p* lines for all the neutral elements lie approximately 0.50 below the *s* lines, which means that the constant *a* in the term formula is 0.50 greater for *p* terms than for *s* terms for a given element.

5. The quantum defects for the series of ionized atoms are less than those of the corresponding neutral atoms.

6. The difference between the *s* and *p* quantum defects becomes less for higher degrees of ionization.

7. The regularities introduced by the increases of Bohr's quantum numbers indicate a possible need for a revision of the theory of the building-up of the atoms of the long periods of the periodic arrangement.

I wish to thank Professor K. T. Compton for his interest and helpful criticism of this work.

Princeton, New Jersey,  
March 5, 1924.

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*Note.*—Professor H. N. Russell has pointed out to me that straight lines will also be obtained if the quantum defects obtained from Bohr's quantum number are plotted against a sequence of integers. For example, one can use for abscissas for Li, 1; Na, 2; K, 3; Rb, 4; Cs, 5. There is no choice between the two methods of plotting on the basis of more accurate satisfaction of the linear relationship for either method. If this be the correct expression of the relationship, it means that the effect of the completion of each group of orbits corresponding to a whole chemical period has the same effect on the quantum defect, even though some of these

groups contain 8 electrons and others 18 or 32. It does not seem probable to me that these groups, so different in number, would influence the quantum defect by the same amount. One advantage of the scheme of changed quantum numbers is that it is in accord with the occurrence of simple spectra in elements in the middle of the longer periods, where the orbits of the next higher total quantum number begin to appear; *i. e.*, if the quantum number of the normal orbit in K is 4, and that of Rb is 6, the intermediate number 5 is in all probability the correct one for the intermediate element of similar spectroscopic type, Cu. The change of 3 units between the quantum numbers of Ba and Ra would lead one to expect two elements with spectra of their type in the period of 32. Hg is one of these, of course. Hicks\* has recently pointed out that lines of the spectrum of Eu indicate that it, too, is of this spectroscopic type. The more complete working out of the spectra of the rare earth elements will throw much light on this question.

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*XLII. The Rotating Earth as a Reference System for Light Propagation.* By L. SILBERSTEIN, *Ph.D.*†

THE relativistic physicist has no difficulty in placing an "observer," with clock and measuring rod, now upon a distant star, now upon an atom or an electron, and reasoning about his experiences. There is certainly nothing illegitimate or contemptible about such fictitious standpoints or reference frames, provided they are helpful in deducing some consequences of a verifiable nature. Yet all such frames or reference systems offer only an indirect interest, and their properties cannot, of course, be explored without the intercalation of a chain of more or less uncertain principles, assumptions, or guesses. There is, however, one frame which can be explored directly and to which, moreover, all our actual observers are chained down, perhaps forever,—and that is our own Earth. The purpose of this paper is to emphasize the need for its experimental investigation as a reference system, especially for optical phenomena, and to state the actual problem without prejudice either against or in favour of Einstein's theory of relativity.

\* W. M. Hicks, 'Nature,' 113, p. 642, May 3, 1924.

† Communicated by the Author. Paper read in the H. A. Lorentz Colloquium held at the University of Wisconsin, Madison, March 30, 1922. Communication No. 212 from the Research Laboratory of the Eastman Kodak Company.

The properties of the Earth as a reference frame for *mechanical phenomena* can be said to be fairly well known. They are anisotropic and symmetrically distributed around an axis practically fixed in the frame, and are typified, say, by the Foucault pendulum, the gyrocompass, and the projectile, whose behaviour is described, for the present at least, with sufficient accuracy by the well-known Newtonian equations of motion written for "rotating axes." If  $\mathbf{r}$  be the position vector of a particle, these equations are condensed in the vector equation, in obvious symbols,

$$\left(\frac{d}{dt} + V\tilde{\omega}\right)^2 \mathbf{r} = \mathbf{F}$$

or, developed,

$$\ddot{\mathbf{r}} = \mathbf{F} - 2V\tilde{\omega}\dot{\mathbf{r}} + \omega^2\mathbf{r} - \tilde{\omega}(\tilde{\omega}\mathbf{r}), \quad . \quad . \quad . \quad (1)$$

where  $\tilde{\omega}$  is a constant vector along the said axis of symmetry (SN) and  $\omega$  its absolute value. Historically, of course, this equation was derived from  $\mathbf{r}' = \mathbf{F}' = \mathbf{F}$ , written for an inertial, say the fixed-stars system  $S'$ , by the familiar relation  $\mathbf{r}' = \mathbf{r} + V\tilde{\omega}\mathbf{r}$ , with  $\tilde{\omega}$  as the spin vector of the Earth relative to  $S'$ , or by the transformation of the cylindrical coordinates  $z' = z$ ,  $\rho' = \rho$ ,

$$\theta' = \theta + \omega t, \quad t' = t. \quad . \quad . \quad . \quad (2)$$

But once in possession of equation (1), we may as well forget its origin and look upon it intrinsically, from a purely terrestrial point of view. It then becomes meaningless, of course, to speak of the Earth's "rotation" (without adding relatively to what). The constant  $\tilde{\omega}$  in (1) is then simply an ascertainable physical directed magnitude belonging to the Earth as such, considered as a reference frame for mechanical phenomena. That the same vector  $\tilde{\omega}$ , with reversed sign, happens to express also the revolution of the starred sky around us (whenever we choose to look up to it), is a most welcome addition to its terrestrial properties, which, however, does not concern us at this stage of the discussion. Of the two supplementary terms in (1) the first, normal to the Earth's axis and the particle's velocity, is known as "the Coriolis force," and the remaining two, amounting together to a transversal vector away from the axis of size  $\omega^2\rho$ , as "the centrifugal force," per unit mass. Thus far the Earth as a mechanical frame.

Our experimental knowledge of the planet as a reference system for *optical phenomena* is, thanks to the famous Michelson-Morley experiment, on the one hand perhaps of a

much more precise nature than the aforesaid, but on the other hand essentially less complete. It can be said without unfairness that what we know about it is just one-half of what seems worth knowing, or just as much as remains to be explored. The information derived from the Michelson-Morley experiment seems as fragmentary as would be our knowledge of the terrestrial mechanical frame if it were limited to experiments of short duration and extending over small distances \*, and what remains to be found out would be the optical counterpart of the behaviour of gyrocompasses and long-range projectiles. In fact, what we have learned from the much discussed and extremely fruitful nil-effect of the Michelson-Morley experiment, stripped of every theoretical interpretation, can be stated as follows:—Let  $O$ ,  $A$ ,  $B$  be three points marked on a slab of stone †. Then, whatever the phase-difference or time-lag between the light-signalling  $OAAO$  and  $OBBO$  in one orientation of the slab, it remains the same for any other orientation, say, after turning the slab by  $90^\circ$ , relatively to the Earth, that is, and no matter at what season of the year. I purposely abstain from calling the slab a “rigid” body. For this would virtually amount to begging the question, and frustrate the desire of stating the result as one of purely phenomenal content divested from every interpretation. For the same reason no mention is made of the possibility of the “distance”  $OA$  or  $OB$  being “shortened” in a certain ratio (Lorentz contraction), whenever the segment is brought by a  $90^\circ$  rotation to a certain otherwise remarkable direction ‡. In fine, the experiment teaches us that there is no privileged direction, that the orientation of the slab is irrelevant. What is responsible for this monotonous, isotropic behaviour is a further question which, at this stage at least, does not interest us.

This, then, is the knowledge of the Earth as an optical reference frame we do possess.

Now, to pass at once to what we do *not* know about it, consider 1, 2, 3, three non-collinear fixed terrestrial stations. Let two light signals be sent simultaneously from 1, one to 2, thence to 3 and back to 1, the other to 3, thence to 2 and back to 1, mirrors being placed at 2 and 3 so as to avoid delay at the stations. The plain question is: *Will both*

\* The former compared with  $2\pi/\omega$ , the day, and the latter with the radius of our planet.

† The support of the interferometer, to be sure, with  $OA$  and  $OB$  roughly “equal” and perpendicular to each other.

‡ That of the resultant of our orbital motion and of the motion of the solar system towards Hercules.

signals return to 1 at the same time or not? And if not, how does the time-lag of one behind the other depend on the circumstances of the experiment, the geometrical properties, the geographic position (presumably only the area and the geographic latitude, respectively), and the inclination of the plane of the triangle 123 to the horizon? It may be interesting to remark that the existence or non-existence of such a time-lag,

$$\Delta = t_{1231} - t_{1321},$$

important on its own account, has also an immediate bearing upon the fundamental question of the possibility of setting up on Earth a consistent clock synchronism based on light signalling, as first proposed by Einstein (1905). For the synchronism thus defined will be *transitive* \*, if and only if  $\Delta = 0$  for every optical circuit.

A reliable and definite answer to these questions can be obtained only from experiment, on a somewhat large scale. Preliminary experiments to that purpose have actually been started by Prof. Michelson at Pasadena in 1921 and are still in progress. Their results, however, may not be available before the end of the summer of 1923 or, perhaps, of the succeeding year.

Theoretically, two different ways of conjecturing the possible outcome of these experiments offer themselves, one based upon the assumption of an æther, the other based upon Einstein's relativity theory, more especially upon the rôle attributed expressly by its founder to the world-geodesics and the minimal lines. With this proviso, the latter method will be shown to lead to a perceptibly definite, unique answer, while the former will give a whole range of possible values of the time-lag, for a given terrestrial optical circuit.

Let us first consider the problem on the æther theory. Without dwelling upon a number of details concerning the shape of light-rays, terrestrial optical trigonometry, etc., which together with the bibliography of the subject were given in a previous paper (Journ. Opt. Soc. of America, v. 1921, pp. 291-307), we may pass at once to the formula covering the only feasible experiment, that is to say, giving the time-lag  $\Delta$  for an optical circuit. If  $-\kappa\tilde{\omega}$  be the relative angular

\* That is to say, the synchronism of clocks at 1 and at 2, and clocks at 2 and at 3, will entail the synchronism of those at 1 and 3. Needless to say that Einstein postulated this transitivity only for inertial systems, and would by no means expect it to hold for the Earth. The subject is here presented as it would be viewed by a radical experimentalist:—Given a reference frame, it is a matter-of-fact question whether an optically established synchronism of its clocks is or is not transitive.

velocity of the æther and the Earth near its surface (so that  $\kappa-1$  will be the rotatory dragging coefficient),  $\sigma$  the area of, say, the triangular circuit, and  $\omega_n$  the component of the spin vector  $\vec{\omega}$  normal to its area, then the required time-lag is

$$\Delta = \frac{4\sigma\kappa\omega_n}{c^2}, \quad . . . . . (3)$$

where  $c$  has its usual meaning. As far as our knowledge goes, the numerical coefficient  $\kappa$  may have any value between 0 and 1. This formula can be easily deduced in a variety of ways. One of these, adopted by the writer (*l. c.* p. 299), is based upon the obvious (approximate) formula

$$\Delta = -\frac{1}{c^2} \int \mathbf{v} d\mathbf{l},$$

already noticed by Professor Lorentz \*, where  $d\mathbf{l}$  is a line-element of the light-path and  $\mathbf{v}$  the relative velocity of the æther, in our case  $\mathbf{v} = \kappa \mathbf{V} \mathbf{r} \hat{\omega}$ . The application of Stokes's theorem gives then (3) at once. Another deduction, which has seemed interesting as being independent of the "ray" or "light-path" concept, is this. For simplicity consider a rotating disk, or a horizontal platform at the north pole. With the centre of rotation  $O$  as origin let  $r_1, r_2$  be the radii vectores of two stations 1, 2, and  $\theta$  the included angle. Let a light signal start from 1 at  $t=0$ . This will spread in the æther as a spherical wave (with the æther point 1 ( $O$ ) as centre), which will reach the second station, *i. e.*, the æther point 2( $t$ ) at an instant  $t$  such that  $ct$  is the third side of the triangle 1( $O$ )O2( $t$ ). Thus, rigorously,

$$c^2 t^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos(\theta + \kappa\omega t),$$

a transcendental equation for the required time of passage  $t=t_{12}$ . In our case,  $\kappa\omega t$  being in all practicable experiments a very small angle, this gives at once, up to  $\omega^2$  terms,

$$ct_{12} = D_{12} + r_1 r_2 \sin \theta \cdot \frac{\kappa\omega}{c},$$

where  $D_{12} = \bar{1}2$ . Similarly,  $ct_{21} = D_{21} - r_2 r_1 \sin \theta \cdot \frac{\kappa\omega}{c}$ .

Whence,

$$t_{12} - t_{21} = \frac{4\kappa\omega}{c^2} \sigma(012), \quad . . . . . (4)$$

where the last factor is the area of the triangle 012. Treating

\* *Wissenschaftliche Abhandlungen*, vol. i. p. 466.

similarly the pair of stations 2, 3, and so on, and adding up the time differences, we shall obtain the previous result with  $\sigma$  equal to the whole area embraced, no matter whether 0 is inside or outside the polygon of stations \*.

Returning to formula (3), divide both sides by  $T$ , the period of oscillation. Then the phase delay per period, or the corresponding shift of the interference pattern with the fringe width as unit, will be

$$\epsilon = \frac{4\sigma\kappa\omega_n}{c\lambda}. \quad (5)$$

A sufficient description of the technicalities of the actual experiment will be found in the paper mentioned above. Here it will be enough to recall that for  $\sigma = 1 \text{ km.}^2$ ,  $\lambda = 5000 \text{ \AA.}$ , and for an angle of  $45^\circ$  between the normal of the triangle plane and the Earth's axis (say, for a horizontal circuit at Chicago), the shift would amount to

$$\epsilon = 1.38\kappa, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

*i. e.*, in the extreme case, of no drag, to about 1.4 fringe widths per each km.<sup>2</sup> embraced by the circuit. (For Pasadena  $\epsilon=1.095\kappa$ .) As to the factor  $\kappa$ , it would be idle to speculate about its value. If there is no rotational drag, then  $\kappa=1$ , if there is a full drag,  $\kappa=0$ , and if a partial one,  $\kappa$  may have any intermediate value. If we are at all to return to the æther concept, then to account for the nil-effect of the Michelson-Morley experiment (which in distinction from the new or *rotational*, may appropriately be referred to as the *translational* terrestrial optical experiment) an almost complete translational dragging of the æther at the Earth's surface must be assumed. In fine, we must have recourse to the Stokes-Planck compressible æther to which Prof. Lorentz devoted an interesting investigation †. But from the translational or annual drag, should it even be complete, no inference can be drawn with regard to a rotational or daily drag of the æther by our planet. Direct data on daily

<sup>\*</sup> Notice in passing that in the transition formula (4) of this proof the area (012) could easily be made enormous, even with the actual stations 1 and 2 not far apart (say only 100 metres at the equator). Unfortunately, however,  $t_{12} - t_{21}$  cannot be made the object of precise measurement (and is even conceptually ill-defined), unlike  $t_{12} + t_{21}$  which is  $t_{21}$ , a local process. This is the reason why at least *three* non-collinear stations (*i.e.*, not eclipsing each other) are indispensable.

+ Cf. Columbia Lectures on 'The Theory of Electrons,' Chap. v. and *Abhandlungen*, vol. i. p. 454. In connexion with recent developments, see also my paper on 'Recent Eclipse Results and Stokes-Planck's Ether,' Phil. Mag. xxxix. Feb. 1920.

aberration, which might throw some light upon this question, are as good as absent, while from Lodge's and Sagnac's experiments, even if they were unimpeachable, one could judge only that there is no æther drag by their comparatively light turn-tables, but not by such massive bodies as the Earth. In fine, as far as is known, the whole interval from 0 to 1 is open to the coefficient  $\kappa$ , and its values may even turn out to be different at different places of the Earth's surface.

Let us now consider the same problem from the standpoint of modern Relativity. Notice that on the classical or Newtonian theory there is no definite connexion, and, in fact, no binding connexion whatever between the properties of the Earth (or any other frame) as a mechanical or kinetical reference system and its properties as a frame for optical phenomena. This is most emphatically shown by the mechanical equation (1) as contrasted with the optical formula (5), the former being perfectly definite, while the latter\* is vague in very wide limits, as broad at least as the range of possible  $\kappa$  values. More generally, there is in Newtonian physics essentially no connexion between mechanics and optics.

In fine, no matter how precise our knowledge of the Earth as a mechanical frame, it leaves us completely in the dark with regard to its behaviour as an optical reference frame, on the classical theory. Not so on the relativity theory, in which optics and kinetics are intimately tied to each other. In fact,—and this is perhaps the most characteristic feature of Einstein's theory,—whatever the quadratic differential form determining the metrical properties of a world domain, its geodesics prescribe the motion of free particles, and the minimal lines of *the same metrical manifold* express the propagation of light in vacuo. In other words, if  $ds$ , given by the form

$$ds^2 = g_{i\kappa} dx_i dx_\kappa,$$

is the appropriate "line-element" for the description of the motion of free particles relatively to any frame  $S$ , through the corresponding geodesics

$$\delta \int ds = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

then *the same line-element* rules also the propagation of light in that system, through the minimal lines

$$ds = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

\* Even apart from the new æther constant  $c$  and the independent introduction of that hypothetical medium at all.



It may, for instance, be very hard to find, for an actual reference frame, the appropriate  $ds$ . But if this be once found, it does both services at the same time: it characterizes the frame as both a mechanical and an optical reference system. The moral of this characteristic feature of Einstein's theory for the case under consideration is obvious.

In fact, the kinetical behaviour of the terrestrial frame is represented with sufficient accuracy by the equation (1) or by the expressions for the centrifugal and the Coriolis forces therein contained. To cover these by the world geodesics substantially, *i. e.* apart from terms immeasurably small, it is imperative to use for the line-element in terrestrial coordinates the form \*

$$ds^2 = \left(1 - \frac{\omega^2 r^2}{c^2}\right) c^2 dt^2 - dr^2 - r^2 d\theta^2 - \frac{2r^2 \omega}{c} d\theta \cdot c dt, \quad (6)$$

which is simply the galileian line-element

$$ds^2 = c^2 dt'^2 - dr'^2 - r'^2 d\theta'^2$$

transcribed from the system  $S'$  to terrestrial co-ordinates by means of the transformation (2). The second-order term  $\omega^2 r^2/c^2$  has been retained only to show this origin of (6). The question of the derivability of the coefficients ( $g_{\mu\nu}$ ) of the quadratic form (6) as the solutions of Einstein's field-equations from huge masses revolving around our abode need not detain us here †. Enough that the form (6) with  $\omega$  equal, of course, to our *full* angular velocity,  $2\pi/\text{day}$ , is essentially indispensable for the correct description of terrestrial kinetics by means of the geodesics (A). Needless

\* It is enough to consider here the two-dimensional case, with  $dz=0$ , that is. The gravitation of the Earth may be altogether disregarded, as its chief effect is only to modify the coefficients of the quadratic terms  $dt^2$  and  $dr^2$ , which is without influence on the rotational optical experiment. The only effect upon a terrestrial optical circuit would be represented by a term amounting, at the utmost (at the equator),

to  $\frac{8}{5} \frac{M}{c^2 R}$ , to be subtracted from the factor 2 in the last (rectangular)

term,  $R$  being the radius and  $M$  the mass of the Earth in astronomical units. Since, however,  $M/c^2 = 0.45 \text{ cm.}$ , this term is of the order  $10^{-4}$ .

† Thirring's attempt at obtaining it is certainly unsatisfactory. According to Einstein's own admission (in a private conversation), the correct values of the centrifugal and the Coriolis force can only be obtained by accepting his cosmological hypothesis of a closed space and uniform mass distribution throughout it. The rotation of the whole universe around us will then give the desired result.

to explain that the approximation we have here in mind corresponds to putting in the final result,  $ds \doteq cdt$ . With this approximation the variation  $\delta r$  yields at once, by (A),

$$\frac{d^2 r}{dt^2} = r \left( \omega + \frac{d\theta}{dt} \right)^2,$$

which exhibits the centrifugal acceleration. Similarly, the variation of  $\theta$  will give the Coriolis term.

Now, such being the  $ds$  required for kinetic purposes, the optical aspect of the terrestrial frame will be completely determined by the principle (B), *i. e.*, dropping the term  $r^2\omega^2/c^2$  which was kept only for formal reasons, by the equation

$$c^2 dt^2 - \frac{2r^2\omega}{c} d\theta \cdot cdt = dl^2, \quad . \quad . \quad . \quad (7)$$

where  $dl = (dr + r^2 d\theta^2)^{\frac{1}{2}}$  is the distance of two terrestrial stations. We need not even solve this equation, etc. in order to see that it leads to all results obtained from the æther-point of view, with  $\kappa = 1$ . For we know beforehand that it was obtained from the  $S'$  equation by the transformation  $\theta' = \theta + \omega t$ . Thus, for instance, light-rays, straight in  $S'$ , will be spiral shaped for terrestrial observers, and so on. (Some curiosities will be found in the paper quoted before.) Thus also the previous shift formula, with  $\kappa = 1$ , must follow. In fact, (7) gives, up to second-order terms,

$$cdt = dl + r^2 d\theta \cdot \frac{\omega}{c},$$

which is identical with the previous formula for  $ct_{12}$ , for infinitesimal  $\theta$ . Whence, as in (4),

$$dt_{12} - dt_{21} = 2r^2 d\theta \cdot \frac{\omega}{c^2} = \frac{4\omega}{c^2} d\sigma,$$

where  $d\sigma$  is the area of the triangle 012.

Thus also the time-lag or corresponding fringe shift for any optical circuit, replacing for the general case  $\omega$  by  $\omega_n$ ,

$$\epsilon = \frac{4\sigma\omega_n}{c\lambda}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

as in (5), but with the particular value  $\kappa = 1$ . Such then is, to a sufficient degree of approximation, the result to be expected on the relativity theory.

There is thus a possibility for discriminating, through the rotational terrestrial optical experiments now conducted by

Michelson, between the relativity- and an æther theory. To state the situation more precisely, if the result of these experiments will be a full shift effect ( $\epsilon=1.38$  per km.<sup>2</sup>, reduced to the stated conditions), there will be no discrimination between the two theories, but this being only one more evasive answer to all questions put to Nature in the name of the æther, it will certainly not help the exiled medium. Should there be, however, either *no* ascertainable shift at all or only a *fraction*  $\kappa$  of the "full" effect, sensibly smaller than unity\*, the relativity theory will be (as Einstein himself gladly admitted) irremediably disproved, while on the æther theory one would have only to assume a complete or partial spinning drag of that medium. This gives the new terrestrial experiment a strong additional interest. As a matter of fact, it was the proof of this possibly crucial nature of the experiment by means of which the writer was fortunate enough to induce Prof. Michelson† to undertake it in spite of the technical difficulties. After what has been explained, it is scarcely necessary to say that by "relativity theory" is here meant the doctrine such as was given to us by Einstein and, if modified, then certainly not so as to give up the concrete (physical) interpretation of either the world-geodesics or the minimal lines. The beauty and conceptual value of Einstein's work as an abstract theory will persist even in the extreme unfavourable case of a nil-effect.

But apart from all such considerations of a possible crucial test, and whatever the final result (nil, fractional, or a full shift), it will undoubtedly be a very desirable contribution to our knowledge of the planet as an optical or electromagnetic system of reference.

Research Laboratory, Eastman Kodak Company,  
Rochester, N.Y.,  
March 15, 1923.

\* Prof. Michelson, who up to the time of this colloquium was not able to discern less than 0.05 of a fringe width, has recently succeeded in pushing this threshold of observability down to 0.01, although the fixing of the "zero" by the control circuit (*cf. loc. cit.*) is thus far somewhat less precise. [In the meantime, November 1923, also the "zero" was fixed by Prof. Michelson to within  $\pm 0.013$  of a fringe width.]

† Who as early as 1904 discussed it on the æther theory. *Cf.* first paper.

**XLIII. *Electron Theory of Aberration and Lorentz Transformations.*** By Dr. D. N. MALLIK, F.R.S.E., Sc.D.,  
Professor of Physics, Aligarh Muslim University, Aligarh,  
India \*.

1. **I**N the usual development of the electron theory of aberration (as given by Poincaré and others), while it enables us to deduce Fresnel's dragging coefficient, it supplies no clue to the Lorentz transformations as a necessary consequence of that theory. In the present paper these transformations are derived as a necessary consequence of the electron theory.

2. Whatever view we may take regarding the physical existence of an æther †, we have to admit, in the present state of science at any rate, that a moving electron produces a magnetic field. If this is granted, we should be justified in regarding the total energy in the Langrangian sense as made up of that of the electrons themselves and that of the field. This procedure was adopted in a paper "On the Theory of Dispersion," in Phil. Mag. April 1915, and, as will be presently shown, directly leads to all the results.

3. Let  $T_1$  = Kinetic energy of an electron,  
 $T_2$  = that of the associated magnetic field, which  
           may provisionally be taken to be that of  
           the æther,  
 $V_1$  = Potential energy due to extraneous forces,  
 $V_2$  = Potential energy of the æther.

Then, if  $x, y, z$  define the position of an electron,

$$\frac{d}{dt} \frac{dT_2}{d\dot{x}} = - \frac{d}{dt} \int (\beta h - \gamma g) d\tau,$$

since

$$- \int (\beta h - \gamma g) d\tau = \text{momentum of the field,}$$

where  $(\alpha, \beta, \gamma)$  = magnetic force,  $(f, g, h)$  = electric polarization, and  $d\tau$  = an element of volume.

\* Communicated by the Author.

† With regard to this, the latest pronouncement of Larmor ('Proceedings of the Cambridge Philosophical Society,' vol. xxi. part iv.) may be quoted:—

"... as is here claimed, closer scrutiny compels a reversion to the view that space is a plenum, is an æther in the historical and ultimate British sense, . . . not a coherent scheme of local physical relations. . . ."

But

$$\int \left( h \frac{\partial f}{\partial z} + g \frac{\partial f}{\partial y} \right) = - \int f \left( \frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} \right) d\tau = - \int f \rho d\tau$$

and (remembering  $4\pi\omega = \frac{\partial\beta}{\partial x} - \frac{\partial\alpha}{\partial y}$ , &c.)

$$\begin{aligned} -4\pi \int (\beta\omega - \gamma u) d\tau &= \int \alpha \left( \frac{\partial\alpha}{\partial x} + \frac{\partial\beta}{\partial y} + \frac{\partial\gamma}{\partial z} \right) d\tau \\ &+ \frac{1}{2} \int \frac{\partial}{\partial x} (\alpha^2 + \beta^2 + \gamma^2) d\tau \text{ (by integration by parts)} = 0, \end{aligned}$$

since

$$\frac{\partial\alpha}{\partial x} + \frac{\partial\beta}{\partial y} + \frac{\partial\gamma}{\partial z} = 0$$

and surface integrals necessarily vanish when taken over the entire field.

Thus

$$\frac{d}{dt} \frac{\partial T_2}{\partial \dot{x}} = - \frac{4\pi}{k_0} \int f \rho d\tau - \int \rho (\gamma \dot{y} - \beta \dot{z}) d\tau.$$

Moreover,

$$\int \frac{\partial T_2}{\partial x} d\tau = \frac{1}{8\pi} \int \frac{\partial}{\partial x} (\alpha^2 + \beta^2 + \gamma^2) d\tau = 0,$$

and

$$\begin{aligned} \frac{2\pi}{k_0} \int \frac{\partial}{\partial x} (f^2 + g^2 + h^2) d\tau &= \frac{\partial V_2}{\partial x} = 0 \\ \left[ \frac{1}{\sqrt{k_0}} = \text{velocity of light in the æther} \right]. \end{aligned}$$

Now the Langrangian equation of motion is of the type

$$\frac{d}{dt} \left( \frac{\partial T_1}{\partial \dot{x}} + \frac{\partial T_2}{\partial \dot{x}} \right) - \frac{\partial (T_1 + T_2)}{\partial x} + \frac{\partial (V_1 + V_2)}{\partial x} = 0;$$

i. e.,

$$\frac{d}{dt} \left( \frac{\partial T_1}{\partial \dot{x}} \right) + \frac{\partial V_1}{\partial x} = \frac{4\pi}{k_0} \int f \rho d\tau + \int (\rho \dot{y} - \beta \dot{z}) d\tau$$

if we admit  $\frac{\partial T_1}{\partial x} = 0$ , i. e. regard electrons to be of invariable size.

Now  $T_1 = \frac{1}{2} (L\dot{x}^2 + m)(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$  for a single electron

of self-inductance  $L$ , mass  $m$ , and charge  $e$ , while

$$\begin{aligned}
 -\frac{\partial V_1}{\partial x} &= \text{force due to system of electrons in a given volume} \\
 &\quad + \text{force brought into play on account of dis-} \\
 &\quad \text{placement } (x-x_0, \text{ \&c.}) \text{ of the electrons,} \\
 &= \frac{4}{3} \pi \frac{A}{k_0} \text{ per unit charge (as in the corresponding} \\
 &\quad \text{magnetic theory) } - \lambda(x-x_0) \text{ (per unit charge).} \\
 &= \frac{4}{3} \pi \int \frac{A}{k_0} \rho \, d\tau - \lambda \int \frac{A}{\rho} \rho \, d\tau \text{ (where } \lambda \text{ is a constant for} \\
 &\quad \text{a small displacement)}
 \end{aligned}$$

since  $\rho(x-x_0) = A$ ,

where  $A, B, C$  are defined by

$$\begin{aligned}
 \frac{\partial A}{\partial x} + \frac{\partial B}{\partial y} + \frac{\partial C}{\partial z} &= -\rho \\
 &= -\left(\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z}\right),
 \end{aligned}$$

i. e.,  $I(A, B, C)$  is the coefficient of electrification, giving rise to electronic moment  $I \, d\tau$ .

4. For the entire system of electrons in volume  $\int d\tau$ , we have, accordingly, equations of the type

$$\begin{aligned}
 \frac{1}{e} \int (Le^2 + m) \ddot{u} \rho \, d\tau + \frac{\lambda}{e} \int A \, d\tau - \frac{4}{3} \pi \int \frac{A}{k_0} \rho \, d\tau \\
 = \frac{4\pi}{k_0} \left[ \int \rho f \, d\tau + \rho(\gamma \dot{y} - \dot{z} \beta) \, \delta\tau \right].
 \end{aligned}$$

Writing  $\rho \ddot{u} = \ddot{A}$ , and taking mean values of the various quantities under the sign of integration, viz.

$$\frac{\int \ddot{A} \, d\tau}{\int d\tau} \equiv \ddot{A}, \quad \frac{\int (A + 3f) \, d\tau}{\int d\tau} \equiv e(A + 3f), \quad \text{\&c.},$$

we have

$$(Le^2 + m) \ddot{A} + \lambda A = \frac{4\pi}{k_0} e^2 \left\{ \left(\frac{1}{3} A + f\right) + (\dot{y} \gamma - \dot{z} \beta) \right\},$$

which can be written in the form

$$\ddot{A}_k + p_k^2 A_k = a_k f$$

if the magnetic effect is omitted or is nil, the suffix referring to the  $k$ th group of electrons.

5. Again, the expression for the energy (as was shown in the former paper) can also be written for a material medium,

$$W = \frac{2\pi}{k} \int (f_0^2 + g_0^2 + h_0^2) d\tau,$$

where  $f_0 = f + A$ , &c.,

and

$$T = \frac{\mu}{8\pi} \int (\alpha^2 + \beta^2 + \gamma^2) d\tau,$$

so that  $\frac{1}{k\mu} = V^2$ , where  $V$  is the velocity of light in the material medium considered.

These lead by the principle of least action, viz.

$$\delta \int (T - W) dt = 0,$$

to

$$\ddot{f}_0 = V^2 \nabla^2 f_0 \quad \text{or} \quad \ddot{f} + \ddot{A} = V^2 \nabla^2 f_0, \quad \&c.$$

6. But if  $X$  = the electrostatic force in the direction of  $x$ , we should have

$$X = \frac{4\pi}{k_0} f = \frac{4\pi}{k} f_0;$$

for it should have the same value, whether we regard it as arising from  $f$  or  $f_0$ .

Hence  $\ddot{f} + \ddot{A} = V^2 \nabla^2 f$ , and two similar equations.

Finally for a plane wave,  $z = \text{const.}$ , we have

$$\ddot{h} + \Sigma \ddot{C}_k = V_0^2 \frac{\partial^2 h}{\partial z^2},$$

together with

$$\ddot{C}_k + p_k^2 C_k = a_k h,$$

where  $C_k$  refers as before to the  $k$ th group of electrons.

7. These suffice for the derivation of the dispersion formula

$$n'^2 - 1 = \Sigma \frac{a_k}{p_k'^2 - p'^2},$$

since we may write

$$h = h_1 e^{ip'(\frac{n'z}{V_0} - t)} \quad \text{and} \quad C = C_0 e^{ip'(\frac{n'z}{V_0} - t)}.$$

It will be observed that since  $\frac{\partial A}{\partial x} = 0$   $\frac{\partial B}{\partial y} = 0$ , we have  $\frac{\partial C}{\partial z} = -\rho$ , and therefore it will suffice to consider the equations involving  $C$  alone.

8. Now if  $x, y, z$  are the coordinates of a point referred to fixed axes, and  $x', y', z'$  those of the same point referred to axes moving with velocity  $0, 0, \zeta$  uniformly, we have

$$x' = x, y' = y, z' = z - \zeta t,$$

and the transformed equations become

$$\ddot{h} + \left( \frac{\partial}{\partial t} + \zeta \frac{\partial}{\partial z} \right)^2 \Sigma C_k = V_0^2 \frac{\partial^2 h}{\partial z^2}$$

and

$$\left( \frac{\partial}{\partial t} + \zeta \frac{\partial}{\partial z} \right)^2 C_k + p k^2 C_k = a_k h$$

(where  $V_0$  = velocity of light in the æther),

since  $f, g, h$  being coordinates of the æther may be held to be unaffected by this motion.

9. Writing now

$$C_k = C e^{p \left( \frac{nz}{V_0} - t \right)} \quad \text{and} \quad h = h_1 e^{ip \left( \frac{nz}{V_0} - t \right)},$$

we have

$$h_1 \{ (ip)^2 - (ipn)^2 \} + \left( ip - \zeta i p \frac{n}{V_0} \right)^2 \Sigma C_0 = 0$$

$$\text{and} \quad \left( ip - \zeta i p \frac{n}{V_0} \right)^2 C_0 + C_0 p k^2 = a_k h,$$

or

$$n^2 - 1 = \left( 1 - \frac{n\zeta}{V_0} \right)^2 \Sigma \frac{a_k}{p k^2 - p^2 \left( 1 - \frac{n\zeta}{V_0} \right)^2}.$$

But

$$p \left( 1 - \frac{n\zeta}{V_0} \right) = p' \quad [\text{art. 11, eqn. (1)}];$$

$$\text{i.e.} \quad \frac{n^2 - 1}{\frac{n'^2}{V_0^2} - 1} = 1 - 2 \frac{n\zeta}{V_0}, \quad \text{nearly,}$$

leaving out square terms in  $\zeta$ .

10. Again, if  $V$  = velocity in the moving medium, and  $V'$  = velocity in the quiescent medium,  $V - V' = \zeta \epsilon$ , where  $\epsilon$  is the dragging coefficient of Fresnel.

But

$$\frac{n}{V_0} = \frac{1}{V} \quad \text{and} \quad \frac{n'}{V_0} = \frac{1}{V'},$$

so that

$$\frac{n - n'}{V_0} = \frac{-\zeta \epsilon}{V V'}.$$



while

$$n+n' = \frac{2V_0}{V'} \quad \text{or} \quad n^2 - n'^2 = -\frac{2\xi\epsilon V_0^2}{V'^2 V};$$

whence

$$\epsilon \frac{n'^2}{V} = (n'^2 - 1) \frac{n}{V_0},$$

$$\epsilon = 1 - \frac{1}{n^2}, \text{ nearly.}$$

11. If, however, the motion is not to affect  $\rho$  (*i. e.* electric charge is to be an invariant, since the element of volume is unchanged on the above scheme of transformation),  $C$  should have the same value in both cases.

But if  $C = C_0 e^{ip(n'z' \sqrt{k_0} - t)}$  in a fixed medium, *i. e.* relative to the moving observer in a moving medium, and  $C = C_0 e^{ip(nz \sqrt{k_0} - t)}$  in a moving medium, relative to a fixed observer ;

on identifying the two expressions (on the understanding that  $z' = (z - \xi t)$ ), we get

$$p'n' = pn \quad \text{and} \quad p'(1 + n'\xi \sqrt{k_0}) = p,$$

or

$$p \left(1 - \frac{n\xi}{V_0}\right) = p'; \quad . . . . . (1)$$

but also

$$\frac{1}{n} = \frac{1}{n'} + \xi \sqrt{k_0}. \quad . . . . . (2)$$

This, however, contradicts the previous result [art. 10], which, as we know, is verified by experiment.

12. This suggests that the equation of transformation should be modified. Let us write, therefore,

$$z' = \lambda(z - \xi t) \quad . . . . . (1)$$

but as even this does not give the right result, we should write further

$$t' = \mu(t - \nu z) \quad . . . . . (2)$$

where  $\lambda, \mu, \nu$  have to be determined.

Thus  $C = C_0 e^{ip(n'z' \sqrt{k_0} - t')}$  relative to the moving observer, moving with the medium,

and  $C = C_0 e^{ip(nz \sqrt{k_0} - t)}$  relative to the fixed observer.

Now comparing coefficients of  $z$  and  $t$ , on identifying the

two expressions, we have

$$\text{and } p'(n'\lambda\sqrt{k_0} + \mu\nu) = pn\sqrt{k_0} \quad (3)$$

$$p'(\lambda\xi\sqrt{k_0} + \mu) = p, \quad (4)$$

giving

$$\frac{\lambda}{\frac{V'}{V} + \mu\nu} = \frac{1}{V} \quad \text{or} \quad V = \frac{\lambda\xi + \mu V'}{\lambda + \mu\nu V'};$$

but  $V = V' + \xi(1 - V'^2 k_0)$  up to the first order [art. 10];

whence

$$\lambda = \mu \quad \text{and} \quad \nu = \xi k_0 = \frac{\xi}{V_0^2},$$

and the equations of transformation become

$$z' = \lambda(z - \xi t), \quad (1')$$

$$t' = \lambda(t - \xi k_0 z). \quad (2')$$

13. The evaluation of  $\lambda$  may be effected by the use of the principle that either medium may be regarded as being in motion in relation to the other. Now, from (1') and (2'), we get

$$\lambda z \left(1 - \frac{\xi^2}{V_0^2}\right) = z' + \xi t',$$

$$\lambda t \left(1 - \frac{\xi^2}{V_0^2}\right) = t' + \frac{z'\xi}{V_0}.$$

But on the above principle,

$$z = \lambda(z' + \xi' t'),$$

$$t = \lambda\left(t' + \frac{z'\xi'}{V_0^2}\right),$$

which gives

$$\lambda = \left(1 - \frac{\xi^2}{V_0^2}\right)^{-\frac{1}{2}}.$$

14. It is easy to verify that if  $\lambda$  has this value, the coefficient of  $\xi^2$  in the period equation vanishes identically.

For, using the above transformation (1') and (2'), the equations of motion become

$$\ddot{h} + \frac{1}{\lambda^2} \left( \frac{\partial}{\partial t} + \zeta \frac{\partial}{\partial z} \right) \Sigma C_k = V_0^2 \frac{\partial^2 h}{\partial z^2}$$

and

$$\frac{1}{\lambda^2} \left( \frac{\partial}{\partial t} + \zeta \frac{\partial}{\partial z} \right)^2 C_k + p_k^2 C_k = a_k h,$$

so that we get

$$(n^2 - 1) = \frac{\left(1 - \frac{n\zeta}{V_0}\right)^2}{\lambda^2} \Sigma \frac{a_k}{p_k^2 - \frac{p^2}{\lambda^2} \left(1 - \frac{n\zeta}{V_0}\right)^2}.$$

But  $\left(1 - \frac{n\zeta}{V_0}\right) \frac{1}{\lambda^2} = 1 - \frac{2n\zeta}{V_0}$  up to  $\zeta^2$ , if  $\lambda = \left(1 - \frac{\zeta^2}{V_0}\right)^{-\frac{1}{2}}$ .

15. The above method of deriving Lorentz transformations might appear to be less elegant than some others, such as that of Laue, but it seems to have the advantage of showing, so far as it goes, the implied dynamical mechanism. Moreover, while the method based on the principle of relativity is mainly kinematical, here we seem to get at the source of the light-signals itself.

16. In the paper above referred to, it was shown that  $f$  and  $f_0$  may be physically interpreted as being of the nature of rotations, thus according well with various elastic solid theories of dispersion. Such a view should therefore fit in with Bohr's theory of atomic structure, but the requisite analysis will have to be held over for the present.

#### XLIV. *Some Cases of Polymorphic Transformation Energies.* By A. HARE, M.Sc.\*

##### *Introduction.*

**A**LTHOUGH the phenomenon of cathodo-luminescence has been the subject of careful investigations for a number of years, and a considerable amount of experimental evidence has been obtained, there has yet appeared no proved general explanation of all the facts.

Experiments † have been carried out in the Physics Laboratories of Leeds University, with the object of determining

\* Communicated by Professor R. Whiddington.

† Ewles, Phil. Mag. vol. xlv. (1923).

whether the luminescence excited by cathode rays appears only when the rays acquire a minimum speed, that is, whether a definite quantum of energy is required to excite the luminescence. With each of the substances tried a definite critical velocity of the cathode rays was found. It was also found that above the temperature of transformation the cathodo-luminescence disappeared. This indicates an intimate relation between the processes involved in the molecular rearrangement and the emission of luminescence. From this the suggestion arose that luminescence is a manifestation of the energy change involved when a substance changes from one state of molecular aggregation to another.

Now, taking the minimum energy required to excite cathodo-luminescence as determined from the formula [ $Ve = \frac{1}{2}mc^2$ ] to represent the quantum of energy required to transform the molecular aggregate, and assuming the equipartition of this energy among the constituent molecules of the aggregate, it should be possible, from a knowledge of this energy and the molecular heat of transformation, to determine the number of molecules composing the aggregate.

The following piece of work was embarked upon in order to measure the energies of transformation of substances showing luminescent properties when bombarded with cathode rays, but, of necessity, substances not showing the above luminescent effects were in some cases used.

#### *Previous Investigations.*

A few results appear in Landolt and Börnstein's tables, but most of these have been calculated by subtracting the heats of formation of the two varieties of substance concerned. Von Hevesey\* performed experiments to determine the heats of transformation of the caustic alkalies KOH, NaOH, RbOH, and CsOH. De Forcrand† investigated the case of zinc oxide, but his determination was based on an indirect chemical method, again involving heats of formation differences, and is in no way similar to the method about to be described.

#### *Experimental Details.*

The scheme involved the use of a furnace, the usual type being used. The vitreous tube was about 70 cm. long and 5 cm. in diameter. The tube and helix were enclosed in a

\* *ZS. Phys. Chem.* lxxiii. p. 683 (1910).

† *C. R.* cxxxiv. p. 1426 (1902).

thick insulating layer of magnesia with an asbestos casing round it. The whole was then placed in a large iron cylinder with terminals to which the strip was connected. A variable resistance and a choking coil were used in series with the furnace. An ampere meter was inserted in the circuit for convenience: the furnace was used in a horizontal position in order to eliminate, as far as possible, the disturbing effects of air convection currents.

In order to keep the temperature of the furnace uniform along the length of the tube, loose asbestos wool was placed in each end of the tube for a distance of about seven inches, while a square tin cap containing asbestos lagging was firmly clamped on each end of the furnace, thus completely surrounding the tube with asbestos. Thermocouples of Pt-PtRh were used, these being calibrated by taking the melting points of standard salts. A potentiometer method was used to measure the E.M.F.'s of the thermocouples, the fundamental principle of which is the adjusting of the electric circuit so that no current flows through the thermocouple. This is accomplished by balancing the E.M.F. generated in the thermocouple by an E.M.F. whose numerical value may be varied at will and measured.

Since the two E.M.F.'s are in opposition, the measurements may be made to have all the advantages of a null or zero method, which is usually desirable in precision work. The principle of the method adopted was one of comparing the heat radiated by the substance whose energy of transformation it was required to measure, with the energy radiated during the same time and under the same conditions by an equal volume of silica. Owing to the difficulty of obtaining data regarding the specific heats of substances at their transformation points it was desirable that this factor should be eliminated.

A small silica vessel was filled with a known weight of silica and fastened securely to a long twin bore rod.

#### *Theory of the Method.*

Assuming Newton's law of cooling over the small range required

$$\text{heat radiated per sec. at } P = K(\Theta - \theta),$$

where  $K$  is a constant.

$$\therefore \quad \text{total heat radiated at } P = \int K(\Theta - \theta) dt = mL,$$

where  $m$  = mass of salt used, and  $L$  = heat of transformation per gram.

Also from the second vessel and contents,

$$\text{heat radiated per sec.} = K(\theta' - \theta).$$

$\therefore$  total heat radiated from second vessel and contents

$$= \int K(\theta' - \theta) dt = \int c d\theta,$$

where  $c$  = thermal capacity of the second vessel and contents.

Now over the range required,  $\theta' - \theta$  is a constant which we will call  $\phi$ : also  $c$  is approximately constant for this range.

$$\therefore K = \frac{c(\theta_1 - \theta_2)}{\phi T},$$

where  $T$  = total time of transformation.

$$\therefore mL = \frac{c(\theta_1 - \theta_2)}{\phi T} \int (\Theta - \theta) dt.$$

Integrating this we get

$$mL = \frac{c(\theta_1 - \theta_2)}{\phi T} \left[ \Theta T - \frac{\theta_a^2 - \theta_b^2}{2} \cdot \frac{T}{\theta_1 - \theta_2} \right]$$

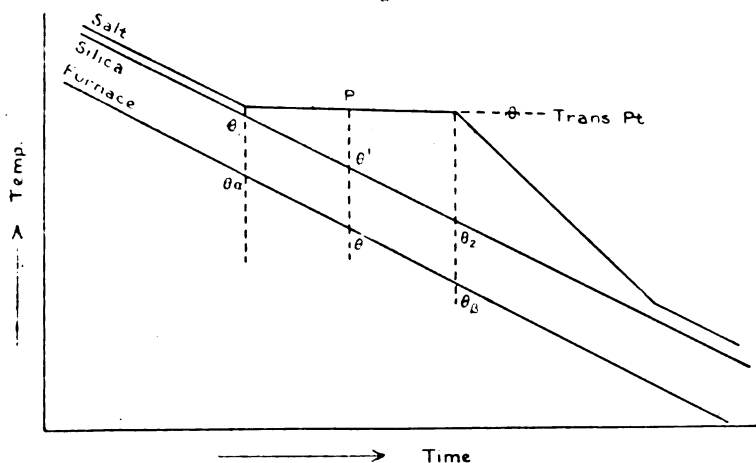
for  $\frac{dt}{d\theta} = \frac{T}{\theta_1 - \theta_2}.$

$$\therefore mL = \frac{c(\theta_1 - \theta_2)}{\phi} \left[ \Theta - \frac{\theta_a + \theta_b}{2} \right],$$

from which  $L$ , the heat of transformation, can be obtained.

These points are brought out in the curves in fig. 1.

Fig. 1.

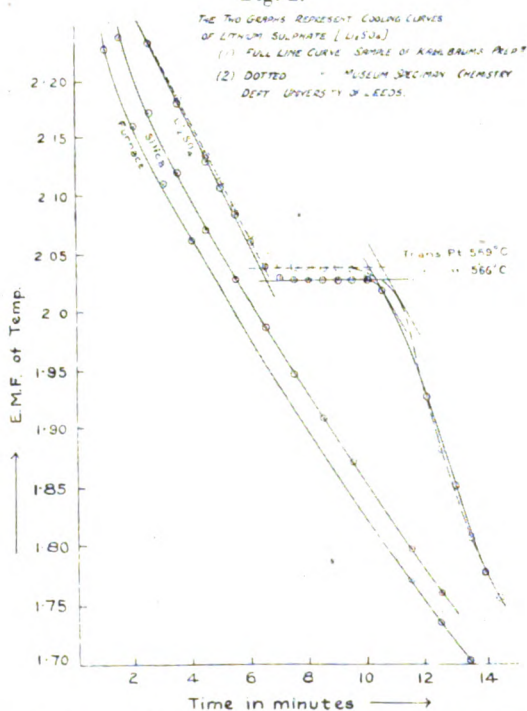


Previously it was customary to limit oneself to an estimation of the transformation point only of a salt, since the

transformation of a substance from one polymorphic state into another was considered to be a comparatively rarely appearing phenomenon.

By making use of a cooling curve an estimate of the transformation heats of various salts can be obtained. At the transformation point, the temperature remains for a time constant during the evolution of heat. Hence the transformation proceeds at a rate governed exclusively by the rate of flow of heat. If this were not the case the temperature would not remain constant for an interval, but would fall

Fig. 2.



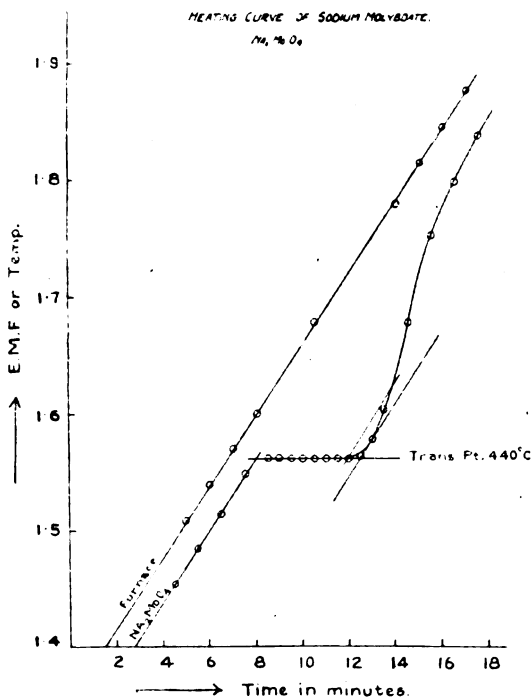
during the change with a diminished speed. With materials having extraordinarily small speeds of transformation, it appears impossible to keep the temperature of the mass constant and in such a case no horizontal part would occur on the cooling curve: merely a decrease in the rate of cooling over a certain temperature interval would be observable. In such cases the method of using cooling curves for fixing transformation points fails.

The theory just given assumes the curves to be ideal, although in actual practice the horizontal portion of the

curve is never so sharply defined, as one would naturally expect. [See figs. 2 and 3.]

The commencement of the transformation is usually well marked; the temperature then remains constant for a certain period, after which the temperature falls, slowly at first, increasing to a maximum and finally at approximately the same rate as the furnace. The end points are brought out with much greater clearness\* by a method employed by Osmond in his original work on the allotropy of iron.

Fig. 3.



According to this author, the end point of the transformation occurs at the point when the temperature difference between the salt and the furnace reaches a maximum. It is also easy to show that this maximum occurs at the point when the perpendicular to the furnace curve is a maximum, or at the point where a tangent drawn parallel to the furnace curve touches the salt curve. At this point it is assumed that all the heat has been evolved. Previous to this point the heat given out by the substance causes the rate of cooling of the

\* 'Dictionary of Applied Physics,' vol. v. p. 438



salt to be less than that of the furnace, while after this point, when all the heat has been evolved, the temperature of the substance falls much more rapidly until, once again, the constant difference in temperature is reached.

At the critical point, the rate of cooling is along the tangent at that point. The heat of transformation can then be calculated from the formula previously mentioned.

### Results.

In order to test the method it has been applied to a re-determination of the known latent heats of substances at high temperatures. The substances chosen were common salt and potassium chloride. The results given for these two substances by the method described agree with those of Plato\*, different weights of the substance being taken in both cases.

The photographic reproduction (fig. 2) of the original graphs for lithium sulphate shows the type of curves.

In this case two samples were taken: (1) prepared by Messrs. Kahlbaum, Berlin, and (2) a museum specimen supplied by the Chemistry Department of the University. The following table shows the results for the substances experimented upon.

Substance.	Melting point in °C.	Latent heat in kg. cal. per gram mol.
Common salt .....	800	1. 7.22 2. 7.14
Potassium chloride.....	772	1. 6.32 2. 6.29
Substance.	Trans. point in °C.	Heat of trans. in kg. cal. per gram. mol.
Potassium sulphate.....	569	2.57
Potassium chromate .....	664	2.45
Lead sulphate .....	806	4.06
Lithium sulphate (1) .....	566	6.77
(2) .....	569	6.96
Sodium molybdate .....	440	14.60
Sodium tungstate .....	579	9.51

In the case of every substance tried, with the exception of sodium molybdate, the heat of transformation could be obtained equally well from either a cooling or a heating curve. This, in effect, means that for these substances the transformation is immediately reversible. In the case of sodium molybdate, however, a time effect was observed.

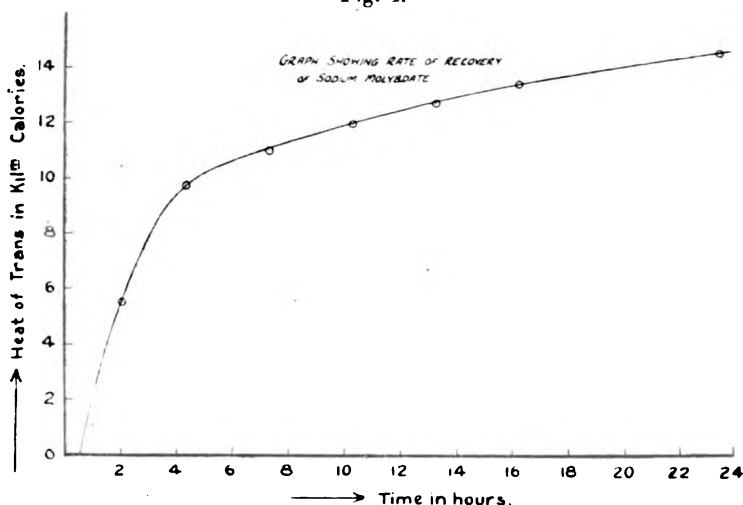
This means that while the transformation could be measured from a heating curve, no effect was observed on

\* Plato, *ZS. Phys. Chem.* 1906.

immediately cooling. This indicates that the transformation does not reverse immediately, but either after a certain interval of time or not at all. Experiments were carried out in order to investigate this point further.

The diagram (fig. 3) shows the curve obtained on heating sodium molybdate, and, as will be seen, is similar in all respects to the cooling curves shown in the case of lithium sulphate. A quantity of sodium molybdate was heated up slightly above the transformation temperatures. When it had all transformed it was taken out of the furnace and kept at room temperature, approximately  $20^{\circ}\text{C}$ . Readings were taken on the substance at intervals of three hours for a period of about twenty-four hours. The readings enabled a curve to be drawn showing the rate of recovery of the substance to its original state after having first been transformed by heating. A reproduction of this curve is given in fig. 4.

Fig. 4.



*Interpretation of Results obtained with  
Sodium Molybdate.*

1. Exponential method.
2. Explanation bearing on a formula, due to Steinmetz, for the characteristic curve of iron.

*Exponential Method.*

The ordinates of the curve (fig.4) represent the heat of transformation in kilogram calories per gram molecule, while the

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abscissæ represent the time in hours. It will be observed that when  $T=0$  the amount of substance recovered equals zero, while when  $T=\infty$  the substance has totally recovered.

The ordinates will be represented by  $M$  and the abscissæ by  $T$  in the following part of the paper.

$\therefore$  when  $T=0, M=0$ ;

and when  $T=\infty, M=M_{\infty}$ ,

where  $M_{\infty}$  = total heat of transformation.

Instead of using the actual curve obtained, a curve was drawn showing the relation between the amount of substance still to be transformed and the time.

Thus when  $T=0, M=0$  and  $M_{\infty}-M=M_{\infty}$ ;

and when  $T=\infty, M=M_{\infty}$  and  $M_{\infty}-M_{\infty}=0$ .

It was then attempted to resolve this curve into a series of exponential terms, the number of terms being limited to two or three.

Two or three exponential terms, however, do not fit such a curve with any great degree of accuracy.

### *Explanation bearing on Characteristic Curve of Iron.*

During the work on the curve satisfying the conditions that when  $T=0, M=0$  and when  $T=\infty, M=M_{\infty}$ , it was noticed that on plotting  $\frac{T}{M}$  against  $T$  a straight line was obtained.

This suggests a formula

$$\frac{T}{M} = a + bT,$$

where  $a$  and  $b$  are constants.

The constants can be calculated by the method of least squares, giving

$$\frac{T}{M} = 0.255 + 0.0596 T.$$

Returning to the equation  $\frac{T}{M} = a + bT$  or  $M = \frac{T}{a + bT}$ , a further constant  $M_0$  is needed to make the equation dimensionally correct. Then  $M = M_0 \cdot \frac{T}{a + bT}$ .

Differentiating this with respect to time we get

$$\frac{dM}{dt} = \left( \frac{a}{M_0} \right) \left( \frac{M}{T} \right)^2 \dots \dots \dots (1)$$

where  $a$  and  $M_0$  are constants.

Now, eliminating  $T$  from the right hand side of the equation,

$$\frac{dM}{dt} = M^2 \cdot \frac{b^2}{M_0 a} - 2M \frac{b}{a} + \frac{M_0}{a}.$$

This can be split into

$$\frac{dM}{dt} = (M - \alpha)(M - \beta),$$

where  $\alpha$  and  $\beta$  are constants.

This is consistent with the view that two monomolecular changes are proceeding at the same time.

It is interesting to note that the equation  $\frac{T}{M} = a + bT$  also fits the characteristic curve in the case of iron.

The phenomenon of magnetization is known to be a breaking up of the molecular aggregates with a definite lagging effect after the force has been removed and appears, therefore, to be a similar problem.

In conclusion, I wish to thank Professor Whiddington for suggesting the problem and for his generous and kindly advice during the carrying out of the work.

The Physics Laboratories,  
The University, Leeds.  
10th June, 1924.

**XLV. *On an Active Modification of Nitrogen.* By M. N. SAHA and N. K. SUR, Allahabad University, Allahabad, India \*.**

**A** FEW years ago Prof. Strutt (now Lord Rayleigh) performed a series of experiments on an active modification of nitrogen †, which excited a good deal of interest at the time. Nitrogen is well known to be an extremely inert gas, but Lord Rayleigh showed that if a condensed spark discharge be sent through  $N_2$ -gas, the glow persists in the gas flowing out of the region of the discharge, which shows considerable chemical and spectral activities. The spectrum of the afterglow was investigated by Fowler and Strutt ‡

\* Communicated by the Authors.

† Strutt, Proc. Roy. Soc. Lond. lxxxv. p. 219; lxxxvi. pp. 56, 105, 262, 529; lxxxvii. pp. 179, 302, 381; lxxxviii. pp. 110, 539.

‡ Fowler and Strutt, Proc. Roy. Soc. Lond. lxxxvi. pp. 105-117.

and shown to consist of the usual  $\alpha$ ,  $\beta$ , and  $\gamma$  groups of positive bands, with a fourth group which was observed for the first time.

The object of the present paper is to show that almost the whole series of observations recorded by Lord Rayleigh can be explained on the basis of Klein and Rosseland's theory\* of inelastic collision of the second type, which has been further developed by Franck† and his students. For convenience of discussion we begin with a short account of this theory.

The experiments on ionization potential and origin of spectra, which were first carried out by Franck, are now matters of common knowledge. They deal with the interchange of energy between freely moving electrons and atoms. A stream of electrons moving with a definite velocity is projected into a mass of gaseous atoms. When an electron happens to pass close to an atom, then, provided the energy of the free electron exceeds a certain limit given by the quantum condition  $eV = h\nu$ , the whole of its energy may be transferred to the valency electrons lying at the outer periphery of the atom. The valency electron is thereby lifted to higher quantum orbits. These states are not stable, and in a short time it reverts to its original position, the excess of energy being set free as monochromatic radiation. Thus the atoms abstract energy from the free electrons, and convert it to energy of its own monochromatic radiation. This process is indicated by kicks in the current-potential curves, as well as by the emission of the characteristic spectrum of the element. When the energy of the bombarding electron is sufficiently large, it may tear off the valency electron from the parent atom. This stage is known as ionization and indicated by an abrupt rise of the current in the current-potential curve.

Hitherto, attention of all workers has been confined to only one side of the problem, *i. e.*, communication of energy by the free electron to the atom. But Klein and Rosseland showed that the reverse process (*viz.*, communication of energy by the excited atom to the free electron) actually takes place in nature on a very large scale, and accounts for a large number of experimental results recorded in previous years. For example, suppose we have a mass of mercury atoms, some of which has been activated either by absorption

\* Klein and Rosseland, *Zs. f. Physik*, iv. p. 46.

† Franck, *Zs. f. Physik*, ix. p. 259; xi. p. 155. Cario, *Zs. f. Physik*, x. p. 105 and p. 166. Compton, *Journal of the Optical Society of America*, 1923.

of the light  $\lambda = 2536$  ( $1S-2p_2$ ) or by an electric discharge from the normal ( $1S$ ) stage to the next stage  $2p_2$ . If, now, an electron passes close to this mercury atom ( $2p_2$  stage), what will take place? According to older conceptions, we could think of no other process than that the electron would communicate its energy to the mercury atom, and excite it to still higher quantum states or to ionization. But Klein and Rosseland pointed out that the reverse process may also take place, viz., the mercury atom may transfer its extra amount of energy corresponding to  $\lambda = 2536$  to the electron. The electron thus receives an increment in its velocity, but the transfer is "*radiationless*," i. e. the electron *chokes the emission* of the light  $\lambda = 2536$ , which would have otherwise certainly taken place. The chance of this "radiationless transfer" depends upon circumstances which are yet to be worked out, but there seems to be no doubt that it is a very general phenomenon\*.

These considerations were further extended by Franck and his students, who showed that the excited atoms may communicate their energy not only to the electron, but also to such atoms or molecules as may come in contact with them. These atoms or molecules will therefore receive either some increment in their kinetic energy or, if the energy imparted be sufficiently large, they may be excited to their spectral emission, ionization or dissociation in the case of molecules.

These ideas, therefore, open up a very promising field of investigation, and Franck has already pointed out, and confirmed several interesting deductions. For example, a stream of mercury gas was excited by  $\lambda = 2536$ , and these activated Hg atoms were allowed to act upon the  $H_2$ -gas. It was proved that the  $H_2$ -gas was thereby dissociated into atoms. The explanation is that when a mercury atom absorbs the light  $\lambda = 2536$ , it is loaded to an energy-content of 4.9 volts. On coming into contact with the  $H_2$ -gas it

\* It may be noted here that Klein and Rosseland were led to this conception from Einstein's idea of "Negative Einstrahlung" or negative absorption. A Hertzian oscillator when placed in a field of radiation may either take up the energy from the field, or give up its own energy to the field, according as the phase difference between the vibration of the resonator and the incident radiant waves is less or greater than  $90^\circ$ . The former case is positive absorption, energy being taken up by the resonator from the field. The latter case is negative absorption, energy being given to the field, just as in alternate current instruments, if the phase difference between the current and potential is  $>90^\circ$ , the work done by the instrument  $EI \cos \phi$  becomes negative, i. e., work has to be done on the instrument.

delivers this energy to the molecule of  $H_2$ , which is thereby broken up into atoms, as the heat of dissociation corresponds to about 3.8 volts (80000–90000 cal.).

*Transference of energy to atoms.*

Hg atoms activated by  $\lambda=2536$  were allowed to act upon vapours of thallium and silver. Only such lines of these vapours were excited for which the energy required is less than 4.9 volts.

*Choking Effect of Inert Gases on Luminous Mercury Vapour.*

Wood\* carried out years ago a number of very interesting experiments on the luminescence of mercury vapour excited by an electric discharge. He found that if inert gases like  $N_2$ ,  $He_2$ , A were added to the luminous Hg-vapour, the luminosity was quenched, the decrease in luminosity being roughly proportional to the amount of gas added. The explanation according to Franck is as follows:—When an activated Hg atom comes into collision with an atom of A or He, then in some cases energy is communicated to the latter. This results simply in an increase of the kinetic energy of the A or the He atom, as the amount of energy transformed (4.9 volts) is quite insufficient to lift the vibrating electron of A or He to the higher orbit. The net result is, therefore, the quenching of the line  $\lambda=2536 \text{ \AA.U.}$  or other lines of the Hg spectrum.

The phenomenon is therefore quite general. If to a mass of luminous gas another gas is added of which the radiation potential is higher than that of the luminous gas, the luminosity is choked.

To those who have followed the work of Lord Rayleigh on active nitrogen, the foregoing discussion would seem to hold out promises of a very satisfactory explanation. But all is not plane sailing as the following discussion will show. We begin with a concise statement of our explanation.

When a moderately condensed discharge is sent through  $N_2$ -vapour it is converted into an excited state, falling just short of dissociation into its constituent atoms. The amount of energy to which the molecule is loaded lies between 8.2 and 8.5 volts. The average life of such an excited atom is of the order of  $10^{-8}$  second. When the excited nitrogen

\* Wood, *Phys. Zs.* xiii. p. 353 (1912).

molecule falls back to the original state, it emits a band-spectrum lying between  $\lambda=1600$  and  $\lambda=1200^*$ .

This band may be called the primary band, and the usual bands lying in the visible region (the positive bands) stand to this in the same relation as the subordinate series of an element stand to the lines of the principal series.

The arguments in favour of this view are as follows:—The spectrum of active nitrogen was investigated by Fowler and Strutt †, and found to consist of the  $\alpha$  and  $\beta$  groups of positive bands, which according to the canal-ray method of Wien ‡ are due to the  $N_2$  molecule. None of the lines of the familiar line-spectrum (attributed by Fowler to  $N^+$ ) were observed. (It is still a moot point whether the lines due to N atom, recorded by Stark and Hartdke §, were present, as the above-mentioned investigations did not extend up to this region.) None of the negative bands, which according to Wien are due to  $N_2^+$ , were present.

The evidence is thus fairly conclusive that  $N_2$ -gas in the afterglow region simply consists of excited  $N_2$  molecules. The experiments of Lord Rayleigh || to detect whether charged particles were present in the afterglow were entirely negative.

It is also clear that the afterglow bands cannot be the primary bands, for unexcited  $N_2$ -gas is completely transparent to this region. It has got an absorption band lying between  $\lambda=1600$  Å.U. and  $\lambda=1200$  Å.U. That the primary band lies in this region is also proved by the experiments of Brandt ¶, who, using the bombarding electron method of Franck, found an abrupt rise of current in the neighbourhood of 8.2 volts. Several kicks were observed in the current-potential curve between 8 and 9 volts, and these were shown by Brandt to be of the nature of band-emission. The primary emission bands therefore lie between  $\lambda=1600$  and  $\lambda=1200$  Å.U., and are present in the afterglow region. But the glass of the quartz vessels in which these experiments are carried out completely masks them.

The visible bands which are actually observed are simply secondary. Their final orbit is also unstable, just as the final orbits corresponding to the Balmer-lines of H are the

\* Lyman, 'The Spectroscopy of the Ultra-Violet,' p. 63.

† Proc. Roy. Soc. Lond. lxxxvi. pp. 105-117.

‡ Wien, *Ann. d. Physik*, lxix.

§ Stark and Hartdke, *Ann. d. Physik*, lvi. p. 303.

|| Strutt, Proc. Roy. Soc. Lond. lxxxviii. p. 183.

¶ Brandt, *Zs. f. Physik*, viii. p. 32.



diquantic unstable orbits. These bands will therefore be emitted only when these orbits have a certain amount of stability.

According to this view, active nitrogen simply consists of the excited nitrogen molecule loaded to the energy of about 8.5 volts (corresponding to about  $1.9 \times 10^5$  calories). Its great activity is due to the ease with which the particle can part with this amount of energy. When foreign atoms or molecules are not present or present only in small amounts, the excited molecule reverts to the normal state after emission of the primary and the secondary (the usual positive) bands. The average life of the excited atom when it suffers no collision is about  $10^{-8}$  sec. \*, but this may be lengthened when the number of collisions is large. This point will be discussed later on.

When foreign substances are present, the energy is mostly communicated in a radiationless transfer. The foreign substance is thereby stimulated either to luminescence or to chemical activity. The following few selected examples will bring out the point clearly.

- (1) Active nitrogen, when passed over sodium, causes not only the  $D_1$  and the  $D_2$  lines, but also the subordinate series lines to flash out.

The amount of energy required for the excitation of the yellow lines is only 2.1 volts, so that the energy delivered by active nitrogen is sufficient, not only for exciting its entire line-spectrum, *but may probably also suffice to ionize it*, as well as the other alkali elements. Lord Rayleigh found that the maximum emission is at the second line of the principal series 3303. This is probably due to the fact that the energy transferred is very large compared with the excitation potential of Na.

\* Wien's method of determining the charge on luminous atoms may be noted here. He allowed a stream of luminous gas to flow out of a canal-ray tube into a space where a vacuum of the order of  $10^{-3}$  to  $10^{-4}$  mm. is continuously maintained by a number of diffusion pumps. In this space, the gas is allowed to pass between two parallel plates which are maintained at a small distance apart at a constant difference of potential. The spectrum of the luminous slit-like region is photographed. Particles which are uncharged show straight spectral lines, while lines due to charged particles are bent one way or the other. The vacuum in the space is so high that no collision takes place amongst the particles. In this way Wien proved that the  $\beta$  groups of positive bands are due to the uncharged  $N_2$  molecules, whereas the bands in the negative glow are due to  $N_2^+$  molecules.

## (2) Action on mercury.

Active nitrogen, passed over Hg-vapour, excites the fundamental line  $\lambda=2536$  ( $1S-2p_2$ ) and lines belonging to the triplet group of the first subordinate and second subordinate series. The  $2P-3D$  line ( $\lambda=5790$ ) and  $2P-3d_2'$  line ( $\lambda=5769$ ) are not excited, hence probably an upper limit to the energy transferred is obtained by assuming that it just fails to excite the  $3D$  level in the Hg-atom. This is 9.4 volts, which is in accordance with our theory.

## (3) Action on magnesium.

Many arc-lines are developed, but neither the line 4481 nor any other spark-line was excited. The arc-line  $\lambda=4703$  ( $1P-4D$ ) was either not excited at all or excited very feebly.

The ionization potential of magnesium is 7.65 volts, and thus active nitrogen would just suffice to ionize magnesium. Active nitrogen passed over Ca, Ba, or Sr, would excite, besides their arc spectrum, also the spark spectrum.

## (4) Hydrogen and the inert gases have no other influence on active nitrogen except a mere dilution of the glow.

This is in accordance with the fact that the minimum excitation potential of these gases is much higher than the maximum energy which can be transferred by active energy.

On the other hand, when helium is activated by an electric discharge, it is capable of storing a large amount of energy ( $e=20.4$  volts) and hence would be found to be an extremely active substance. This view is supported by an interesting observation of Lord Rayleigh\* in a recent paper, who found that activated helium on coming into contact with  $N_2$ -gas (unexcited) excites the afterglow. If the present view is correct, it would excite not only the positive bands but also the line-spectrum due to N. This point ought to be further investigated.

We now come to the most formidable difficulty confronting the above explanation, viz., chemically pure nitrogen shows no afterglow at all. This matter forms the subject matter of a very interesting paper by Lord Rayleigh in vol. xci. of the P. R. S. London. Following experiments by Tiede and Domeke, who found that chemically pure nitrogen, prepared by heating barium and potassium azide, and carefully freed from all impurities, shows no afterglow at all, Lord Rayleigh showed that nitrogen purified by prolonged standing over

\* Lord Rayleigh, Proc. Roy. Soc. Lond. vol. cii. p. 454.

the liquid alloy of Na and K gave an afterglow, which was however very faint. On introducing small impurities of oxygen, or almost any easily excitable gas (1 in 1000 parts), the glow was restored to full brilliancy. This observation has also been confirmed by recent experiments of Pirani\*, who claims for his nitrogen a purity of  $5 \times 10^{-5}$  per cent. Pirani finds that perfectly pure  $N_2$  shows no luminescence at all, though admixture of electronegative gases like  $O_2$ ,  $H_2O$ ,  $I_2$  in concentration of  $1.5 \times 10^{-3}$  give a maximum after-luminescence. Large admixtures, say from  $6$  to  $8 \times 10^{-3}$ , choke the luminescence. In all these experiments, the authors seemed to have looked only for the after-luminescence of the chemically pure gas as a test of activity. They did not evidently apply the chemical tests. This point is of some importance, because the afterglow is simply the sign of the return of the molecule from the higher quantum states to one of the intermediate unstable states; it does not indicate the reversion to the normal state. Hence, if under certain conditions the intermediate orbits (*i. e.* final orbits of the afterglow band) be not stable, these will not be emitted at all, though the gas will exhibit all the chemical and spectral activity recorded by Lord Rayleigh.

It seems to be a general phenomenon that the activated atom, when left to itself, has always a tendency to fall to the lowest quantum state, without stopping at the intermediate stages. Hence only the primary bands would be emitted. This is confirmed by an interesting investigation of Wood†, who finds that in his discharge-tubes, Balmer lines of H (for which the final orbit is an unstable orbit) are always rendered very brilliant if  $H_2O$  vapour is present as an impurity. The subject is, however, well worth further investigation.

Our explanation of the absence of afterglow in active nitrogen, if true, would mean that nitrogen may be loaded to an energy of about 8.5 volts without being luminous, and therefore will still possess all other properties associated with active nitrogen.

\* Pirani, 'Chemical Abstracts,' 1923, ii. p. 157.

† Wood, Phil. Mag. xlii. p. 729.

XLVI. *Faraday's "Magnetic Lines" as Quanta.*—Part II.  
By Prof. H. STANLEY ALLEN, M.A., D.Sc.\*

INTRODUCTION.

PART I. of the paper bearing the above title was published in the *Philosophical Magazine* for October 1921. At the Edinburgh meeting of the British Association in that year, I gave an account of the principal results of the paper and exhibited the mechanical model to be described in the present communication. At the same meeting Prof. E. T. Whittaker discussed electromagnetic tubes of force in four dimensions, pointing out that the ordinary electrostatic and magnetic tubes were dependent on the relative state of rest or motion of the observer. These results, which were subsequently developed in an important paper read before the Royal Society of Edinburgh †, led me to withhold from publication the material already prepared for Part II. of my own paper. It appeared to me, as I suggested at the time ‡, that it might be necessary to regard the four-dimensional tubes, or "calamoids," of Prof. Whittaker as the true units required by the quantum theory. This view was strengthened in conversation and correspondence with Prof. Whittaker. Further consideration, however, has inclined me to believe that, even though there may be advantages in regarding calamoids as Quanta, there is still something to be learnt from the more familiar magnetic tubes in three dimensions. Two factors have influenced me in coming to this conclusion. In the first place, Prof. Whitehead, whose authority on the philosophical aspects of relativity is undoubted, has stated recently § :—"The aim of the Einstein theory is to derive physical laws of such a general character as to be independent of the peculiarities imposed on measurements by the particular circumstances in which they are made. But this is an arbitrary demand: it may well be that those peculiarities are expressions of the essential realities underlying the phenomena." In the second place, Leigh Page || in an interesting paper has distinguished between "intrinsic magnetic fields," which cannot be annihilated by the

\* Communicated by the Author.

† *Proc. Roy. Soc. Edin.* xlii. p. 1 (1921).

‡ *'Nature,'* cviii. p. 341 (1921).

§ *Proc. Phys. Soc. Lond.* xxxvi. p. 193 (1924).

|| *Phys. Rev.* xxii. p. 188 (1923).

Lorentz transformation, and fields which depend on the observer's state of rest or motion.

In his Report on "The Quantum Theory" (1923) \* Prof. E. P. Adams has devoted a chapter to a discussion of the possibility of a magnetic interpretation of the theory. This contains a useful summary of the work done and of the present position of the problem.

It was shown in Part I. that when a charge  $e$  is moving in an orbit of any shape whatever with high frequency  $\nu$ , there is, associated with each canonical coordinate a magnetic flux of an integral number of quantum tubes, the unit tube being defined by the ratio  $h/e$ , where  $h$  is Planck's constant. There is a magnetic flux through the orbit which may be considered as constituted by a definite whole number of discrete magnetic tubes defined as above. It is of interest to see whether the ideas suggested by the simple cases already dealt with can be applied to more complex distributions. This question is discussed in the first half of the present paper.

In § 1 and § 2 I reproduce the work on quantum magnetic tubes for two current circuits, substantially as it was written in 1921, although I recognize that the method of applying the quantum conditions is open to serious criticism. The results obtained are, however, justified by the more rigorous treatment given in § 3, for which I am indebted to Prof. C. G. Darwin. The extension to any number of current circuits is discussed in the following section. The second half of the paper is concerned with a somewhat speculative attempt to apply the results obtained to Bohr's theory of spectral series.

## 1. QUANTUM TUBES FOR TWO CURRENT CIRCUITS.

We consider as a typical case of a more complex distribution two current circuits, which may be thought of as representing either two magnetons or two electron orbits. The electrokinetic energy is given by the well-known expression

$$\frac{1}{2}L_1i_1^2 + \frac{1}{2}L_2i_2^2 + M_{12}i_1i_2, \quad \dots \quad (1.1)$$

where  $i_1$  = current in the first circuit,  
 $i_2$  = current in the second circuit,  
 $L_1$  = self-inductance of the first circuit,  
 $L_2$  = self-inductance of the second circuit.  
 $M_{12}$  = mutual inductance of the two circuits.

\* Bulletin of the National Research Council, No. 39, Washington.

This may be re-written in the form

$$\frac{1}{2}(L_1 - M_{12})i_1^2 + \frac{1}{2}(L_2 - M_{12})i_2^2 + \frac{1}{2}M_{12}(i_1 + i_2)^2, \quad (1.2)$$

to which it is proposed to apply the quantum conditions.

The quantum theory requires that, when the kinetic energy of a system is expressed in the form

$$\begin{aligned} & \frac{1}{2}A_1\dot{q}_1^2 + \frac{1}{2}A_2\dot{q}_2^2 + \dots \\ & \equiv T_1 + T_2 + \dots \quad (1.3) \end{aligned}$$

( $q_1, q_2, \dots$  being Hamiltonian positional coordinates), the discontinuous energy exchanges always occur in such a way that the steady motions satisfy the equations

$$\left. \begin{aligned} 2 \int T_1 dt &= n_1 h, \\ 2 \int T_2 dt &= n_2 h, \\ &\dots \end{aligned} \right\} (n_1, n_2, \dots \text{integers}), \quad (1.4)$$

the integration in each case being extended over the corresponding period.

It must be observed that the expression (1.2) for the electrokinetic energy differs from (1.3) in the fact that the third term contains the square of  $i_1 + i_2$ , a quantity which depends on the variables  $i_1$  and  $i_2$  involved in the first two terms. Consequently, we are not strictly entitled to use the quantum conditions (1.4).

These conditions were first stated by W. Wilson\*, and are equivalent to those used by Sommerfeld† in discussing the fine structure of spectral lines.

With the above reservation the quantum conditions in the present case may be written

$$\left. \begin{aligned} \int (L_1 - M_{12})i_1^2 dt &= n_1 h \\ \int (L_2 - M_{12})i_2^2 dt &= n_2 h \\ \int M_{12}(i_1 + i_2)^2 dt &= n_{12} h \end{aligned} \right\} (n_1, n_2, n_{12} \text{ integers}) \quad (1.5)$$

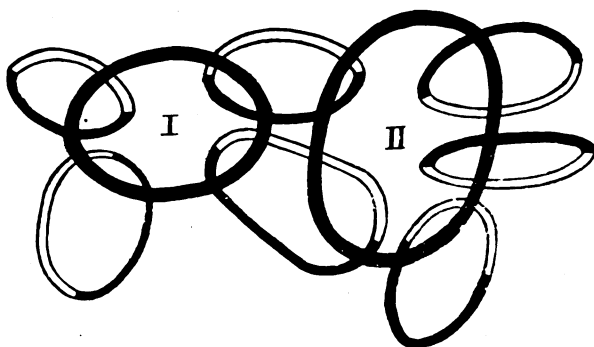
Now, defining magnetic tubes in the way customary in electromagnetic theory,  $L_1 i_1$  is the number of magnetic tubes passing through circuit 1 due to its own current, and  $M_{12} i_1$  is the number of tubes passing through circuit 2 due to the current in circuit 1. The difference between these

\* W. Wilson, *Phil. Mag.* xxix. p. 795 (1915); xxxi. p. 156 (1916).

† Sommerfeld, *Ann. d. Physik*, li. p. 194 (1916).

gives the number of tubes that are linked *only* with circuit 1 (see fig. 1).

Fig. 1.



Magnetic tubes associated with two current circuits.

The two current circuits I. and II. are shown in black. In this case

$N_1$ , the number of tubes linked only with circuit I. is 2,

$N_2$ , the number of tubes linked only with circuit II. is 3,

$N_{12}$ , the number of tubes linked with both circuits is 2,

$N_1$ , the total number of tubes linked with circuit I. is 4,

$N_2$ , the total number of tubes linked with circuit II. is 5,

whilst the total number of tubes in the diagram is 7.

Thus  $L_1 i_1 - M_{12} i_1 = N_1 =$  number of tubes linked  
only with circuit 1. . . (1.6)

Again  $L_2 i_2 - M_{12} i_2 = N_2 =$  number of tubes linked  
only with circuit 2. . . (1.7)

And  $M_{12}(i_1 + i_2) = N_{12} =$  number of tubes linked  
with both circuits . . . (1.8)

It may be remarked that the *total* number of tubes is

$$L_1 i_1 + L_2 i_2 = N_1 + N_2 + N_{12}. \quad (1.9)$$

Also the total number of tubes linked with circuit 1 is  $L_1 i_1 + M_{12} i_2 = N_1$ , and the total number of tubes linked with circuit 2 is  $M_{12} i_1 + L_2 i_2 = N_2$ , results which will be required later.

With this notation the quantum conditions become

$$\left. \begin{aligned} N_1 \int i_1 dt &= n_1 h \\ N_2 \int i_2 dt &= n_2 h \\ N_{12} \int (i_1 + i_2) dt &= n_{12} h \end{aligned} \right\} . . . (1.10)$$

Now,  $\int i_1 dt$  integrated over a complete period represents the total quantity of electricity passing round the circuit, and, according to the electron theory, this must be an integral number of times the electron charge, or  $=k_1e$ , where  $k_1$  is an integer.

In this way we obtain the results

$$\left. \begin{aligned} k_1 N_1 e &= n_1 h \\ k_2 N_2 e &= n_2 h \\ k_{12} N_{12} e &= n_{12} h \end{aligned} \right\}, \quad . \quad . \quad . \quad . \quad (1.11)$$

where  $k_1, k_2, k_{12}$  are integers.

The only difficulty which presents itself here is with regard to the limits to be assigned to the integration in  $\int (i_1 + i_2) dt$ . This question may be elucidated by means of a mechanical analogy to be considered in the following section.

The quantum conditions may be written

$$\left. \begin{aligned} N_1 &= \frac{n_1}{k_1} \left( \frac{h}{e} \right) \\ N_2 &= \frac{n_2}{k_2} \left( \frac{h}{e} \right) \\ N_{12} &= \frac{n_{12}}{k_{12}} \left( \frac{h}{e} \right) \end{aligned} \right\} . \quad . \quad . \quad . \quad . \quad (1.12)$$

The simplest interpretation of these results is to assume the existence of discrete quantum tubes of magnetic induction determined by the ratio  $h/e$ . In Bohr's later theory of atomic structure the several electrons of the complex atom, instead of forming rings as in the earlier model, are supposed to be moving each in its own independent orbit. Thus, in general, in an atomic or molecular system,  $k_1, k_2$ , and  $k_{12}$  will be unity. Even were this not so in a particular case, the value of  $n$  might be supposed an integral multiple of the corresponding  $k^*$ .

## 2. A MECHANICAL MODEL FOR TWO CURRENT CIRCUITS.

In a letter dated Christmas 1876, Clerk Maxwell † wrote : "I have been making a mechanical model of an induction

\* The possibility of the existence of "half-quanta," which have been assumed by several investigators within recent years, may be bound up with the occurrence of the fractions  $n/k$ .

† Campbell and Garnett, 'Life of James Clerk Maxwell,' pp. 396-551 (1882).



coil, in which the primary and secondary currents are represented by the motion of wheels, and in which I can symbolize all the effects of putting in more or less of the iron core, or more or less resistance and Leyden jars in either circuit."

This model, of which a copy is preserved in the Cavendish Laboratory, Cambridge, and another in the George III. Museum of King's College, London, is described and illustrated in Maxwell's biography and in Webster's 'Electricity and Magnetism' (p. 140) \*. The essential part of the mechanism is a differential train of wheels, such as is often employed as a dynamometer and is now familiar in connexion with a motor car. The primary and secondary circuits are represented by two circular disks mounted so as to turn independently about horizontal axes in the same straight line. On the shaft of each disk is mounted a bevel wheel, A and B in fig. 2, and these gear into a third bevel wheel D, which turns loosely on a shaft at right angles to the former pair. This shaft itself, which carries a system composed of four projecting arms of adjustable moment of inertia, can rotate about the same horizontal line as the two disks. A and B can turn independently of each other, except in so far as they are connected through D. Thus the two disks are in mechanical connexion exactly as the driving wheels of a motor car are connected through the differential gearing.

The resemblance between the mechanical and the electrical systems is best seen by writing down expressions for the kinetic energy. Let  $I_1, I_2$  be the moments of inertia for the disks,  $I_{12}$  the moment of inertia for the central system. Let  $\omega_1, \omega_2, \omega_{12}$  be the corresponding angular velocities. The kinetic energy of the mechanical system is

$$\frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}I_{12}\omega_{12}^2. \quad (2.1)$$

In the actual model the bevel wheels are all alike, and the angular velocity of the central part is the mean of the angular velocities of the disks, or  $\omega_{12} = \frac{1}{2}(\omega_1 + \omega_2)$ . In this case the kinetic energy can be written in the form

$$\frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}\frac{I_{12}}{4}(\omega_1 + \omega_2)^2. \quad (2.2)$$

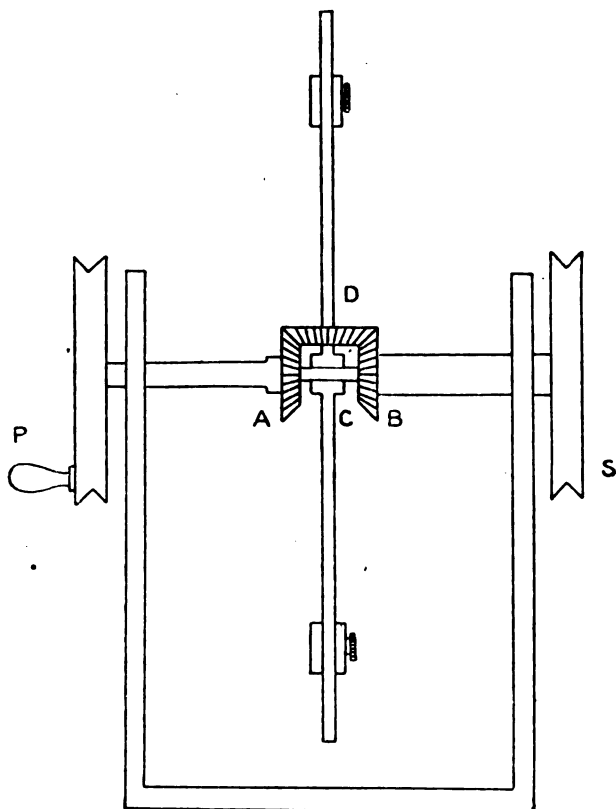
\* The same mechanical analogy has been applied to coupled oscillating circuits by Pomey, *Rev. Gén. d'El.* i. p. 83, Jan. 1917; p. 163, Feb. 1917.

Comparing this with the expression,

$$\frac{1}{2}(L_1 - M_{12})i_1^2 + \frac{1}{2}(L_2 - M_{12})i_2^2 + \frac{1}{2}M_{12}(i_1 + i_2)^2, \quad (1.2)$$

for the electrokinetic energy of two current circuits, we see that the currents are represented in the model by angular velocities, the inductances by moments of inertia.

Fig. 2.

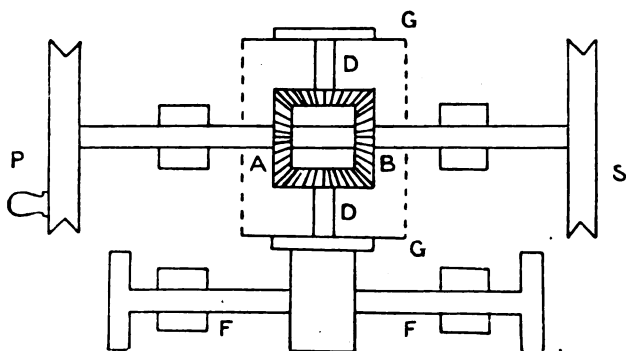


With the object of producing a closer correspondence between the electrical and the mechanical systems, I have devised a modification of Maxwell's mechanism. In this modified apparatus there are three shafts A, B, and F, so connected that the angular velocity of the third shaft F is the algebraic sum of the angular velocities of the independent side shafts A and B, giving

$$\omega_{12} = \omega_1 + \omega_2. \quad (2.3)$$

The shaft which carries the bevel wheels DD is attached to the gear-case, and these all rotate with angular velocity  $\frac{1}{2}(\omega_1 + \omega_2)$ . To effect the desired result it is only necessary to make the gear-case drive the shaft F at double its own speed. This may be done by a belt or chain drive, or by means of pinion wheels as in the model shown in fig. 3.

Fig. 3.



The kinetic energy of the modified mechanism\* is given by

$$\begin{aligned} & \frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}I_{12}\omega_{12}^2 \\ &= \frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 + \frac{1}{2}I_{12}(\omega_1 + \omega_2)^2. \quad \dots (2.4) \end{aligned}$$

This expression is exactly analogous to

$$\frac{1}{2}(L_1 - M_{12})i_1^2 + \frac{1}{2}(L_2 - M_{12})i_2^2 + \frac{1}{2}M_{12}(i_1 + i_2)^2, \quad \dots (1.2)$$

which represents the electrokinetic energy of two current circuits. The currents are still represented in the mechanical system by angular velocities, the inductances by moments of inertia, but in this model the mutual inductance corresponds directly to the moment of inertia of the third shaft. The angular momenta of the three parts of the mechanism correspond to the number of magnetic tubes linked with the primary circuit, the secondary circuit, and the two circuits, respectively. The resemblance between the mechanical model and the current circuits in this latter respect is of special interest, seeing that according to Nicholson's quantum hypothesis angular momentum can be expressed as an integral number of times the unit  $h/2\pi$ , whilst according to the present suggestion the magnetic tubes are multiples of a discrete quantum tube defined by  $h/e$ .

\* The amount of inertia of the gear-case is supposed negligibly small in comparison with that of a shaft.

Returning now to the quantum conditions in (1.10), let us suppose that in finding the value of the integral  $\int (i_1 + i_2) dt$  in the steady state, the integration is extended over the complete period,  $1/\nu_{12}$ , corresponding to the time of revolution of the third shaft of the modified mechanism with angular velocity  $\omega_{12} = \omega_1 + \omega_2$ . Then  $\nu_{12} = \nu_1 + \nu_2$ , and the value of the integral is

$$\frac{i_1 + i_2}{\nu_{12}} = \frac{k_1 \nu_1 + k_2 \nu_2}{\nu_1 + \nu_2} e. \quad (2.5)$$

Provided  $k_1 = k_2 = k_{12}$ , this would give as the value of the integral,  $k_{12}e$ , leading to the result  $k_{12}N_{12}e = n_{12}h$ , already suggested in (1.11).

### 3. PROF. DARWIN'S TREATMENT FOR TWO CURRENT CIRCUITS.

The method of applying the quantum conditions employed in § 1 is unsatisfactory, because the system is one of two degrees of freedom, and so, according to accepted principles, cannot have more than two quantum numbers. I am indebted to Prof. C. G. Darwin for the following treatment, but have made slight alterations in his notation to suit the present case.

To quantize 
$$W = \frac{1}{2}a\dot{x}^2 + f\dot{x}\dot{y} + \frac{1}{2}b\dot{y}^2, \quad (3.1)$$

where the cycles for  $x$  and  $y$  are from 0 to 1.

Put 
$$\left. \begin{aligned} p_x &= a\dot{x} + f\dot{y}, \\ p_y &= f\dot{x} + b\dot{y}. \end{aligned} \right\} \quad (3.2)$$

Then 
$$W = \frac{1}{2} \frac{bp_x^2 - 2fp_xp_y + ap_y^2}{ab - f^2} \quad (3.3)$$

The motion is therefore

$$\frac{dp_x}{dt} = -\frac{\partial W}{\partial x} = 0, \text{ etc., } \dot{x} = \frac{\partial W}{\partial p_x}, \text{ etc.,} \quad (3.4)$$

or 
$$p_x = \text{constant.} \quad (3.5)$$

Hence  $\oint p_x dx = p_x$ , as the  $x$  cycle is 0 to 1.

The quantization is thus

$$p_x = \tau_1 h, \quad p_y = \tau_2 h \quad (\text{where } \tau_1, \tau_2 \text{ are integers}), \quad (3.6)$$

and 
$$W = \frac{1}{2}h^2 \frac{(b\tau_1^2 - 2\tau_1\tau_2 + a\tau_2^2)}{ab - f^2} \quad (3.7)$$

Applying this method to the two current circuits, for which the electrokinetic energy is

$$W = \frac{1}{2} L_1 i_1^2 + M_{12} i_1 i_2 + \frac{1}{2} L_2 i_2^2$$

and the value of  $\oint di$  over a complete period is  $\kappa e$  (where  $\kappa$  is an integer), we find

$$\left. \begin{aligned} \kappa_1 e (L_1 i_1 + M_{12} i_2) &= \tau_1 h \\ \kappa_2 e (M_{12} i_1 + L_2 i_2) &= \tau_2 h \end{aligned} \right\} \dots \dots \dots (3.8)$$

It has already been pointed out that  $L_1 i_1 + M_{12} i_2$  or  $N_1$  is the total number of magnetic tubes linked with the first circuit, and  $M_{12} i_1 + L_2 i_2$  or  $N_2$  is the total number of magnetic tubes linked with the second circuit. Thus the quantum conditions reduce to

$$\left. \begin{aligned} N_1 &= \frac{\tau_1}{\kappa_1} \left( \frac{h}{e} \right) \\ N_2 &= \frac{\tau_2}{\kappa_2} \left( \frac{h}{e} \right) \end{aligned} \right\} \dots \dots \dots (3.9)$$

As in the previous work the simplest interpretation which can be given to these results is obtained by assuming the existence of discrete quantum tubes of magnetic induction, the unit tube being defined by the value of  $h/e$ .

Reviewing the work of §1 in the light of this more rigid treatment, it may be argued that the methods there employed are justified by the results obtained. The explanation of all the difficulties is to be found in the simple fact, illustrated in fig. 1, that the various magnetic tubes associated with two current circuits may be grouped together in several different ways. The relations between the different quantum numbers revealed by this discussion are suggestive in connexion with results derived from investigations on the complex structure of multiplets, especially as regards the Zeeman terms in strong and weak magnetic fields. Reference may be made to the work on this subject published in the past three years, principally by Landé, Pauli, and Sommerfeld.

#### 4. EXTENSION TO ANY NUMBER OF CURRENT CIRCUITS.

In the case of a heavy atom Bohr's later theory postulates the existence of a large number of independent electron orbits. The work of Ellis and others suggests that quantum relations hold even within the nucleus, which may be composed of protons and negative electrons in orbital motion. On this view an atomic and also a molecular system is an

extremely complex system of orbits, in which positively or negatively electrified particles are circulating at high speed, thus virtually constituting a system of current circuits.

There is no great difficulty in extending the results for two current circuits, obtained in 1921 and given above, to the general case of any number of such circuits. For the electrokinetic energy of any system of currents is equal to one-half the sum of the strengths of each current multiplied by the total flux of magnetic force through its own circuit in the positive direction. Following out the same line of argument as before, it would seem that we are led again to the conception of quantum tubes of magnetic induction of strength  $h/e$ , and possessing electrokinetic energy of amount  $\frac{1}{2}h\nu$ , where  $\nu$  is a frequency characteristic of the particular tube considered.

Instead, however, of writing down the equations for the general case and proceeding as in the previous section, it will be more instructive to consider a single Faraday tube of magnetic induction linked with  $n$  current circuits,  $i_1, i_2, \dots i_n$ .

The energy associated with such a tube can be expressed as

$$\int \frac{\mu H^2}{8\pi} A ds \dots \dots \dots (4.1)$$

integrated over the length of the tube, where  $A$  is the area of the cross-section of the tube and  $ds$  is an element of its length. But  $\mu HA$  is constant along the whole length, so that the expression becomes  $\frac{\mu HA}{8\pi} \int H ds$ . The line integral of magnetic force along the length of the tube is

$$4\pi(i_1 + i_2 + \dots + i_n),$$

so that the energy is given by

$$T = \frac{1}{2} \mu HA (i_1 + i_2 + \dots + i_n). \dots \dots (4.2)$$

We now assume that the quantum condition may be expressed in the form

$$2 \int T dt = nh \quad (n \text{ integral}),$$

$$\text{or} \quad \mu HA \int (i_1 + i_2 + \dots + i_n) dt = nh, \dots \dots (4.3)$$

the integration for each current extending over the corresponding period\*.

\* It is hardly necessary to point out that this way of stating the quantum conditions is somewhat arbitrary, but so is any statement of these conditions, which must be regarded rather as a set of rules justified by the results obtained than as a consistent and unique theory.

This gives

$$\mu HA(k_1 + k_2 + \dots + k_n)e = nh. \quad (4.4)$$

Here, again, the simplest interpretation is to assume

$$n = k_1 + k_2 + \dots + k_n,$$

so that the unit tube is defined by taking

$$\mu HA = h/e. \quad (4.5)$$

The electrokinetic energy of the unit quantum tube in question is given by

$$\frac{1}{2} \frac{h}{e} (i_1 + i_2 + \dots + i_n)$$

$$= \frac{1}{2} h (k_1 \nu_1 + k_2 \nu_2 + \dots + k_n \nu_n), \quad (4.6)$$

since we may write

$$i_1 = k_1 e \nu_1, i_2 = k_2 e \nu_2, \dots i_n = k_n e \nu_n.$$

Proper attention must, of course, be paid to the sign of each term.

Thus when  $k_1 = k_2 = \dots = k_n = 1$ , the electrokinetic energy of the unit tube

$$= \frac{1}{2} h (\nu_1 + \nu_2 + \dots + \nu_n). \quad (4.7)$$

The importance of this mode of expression lies in the fact that *frequency* here plays the part of an additive quantity in formulating the energy of a system. This is a characteristic feature of Bohr's theory of spectral series, and in the next Section an attempt will be made to apply the result to the interpretation of Bohr's theory.

## 5. APPLICATION TO THE THEORY OF SPECTRAL SERIES.

Sir William Bragg in the Kelvin Lecture \* delivered before the Institution of Electrical Engineers on January 13, 1921, said: "The frequencies of the lines in a spectrum often display curious and exact numerical relations, in the form generally involving differences of frequencies of similar lines or groups of lines. . . .

"Now, there is nothing in our older conception of the origin of radiation within the atom to give us a clue as to why differences of frequencies should come into these empirical, though most useful, formulæ. We have pictured to ourselves vibrating systems, mechanical or electric, and waves arising therefrom. But what connexion between masses or electricities gives us in any simple way equations

\* 'Nature,' cxcvii. pp. 82-109 (1921).

involving the addition or subtraction of frequencies? We are in a blind alley."

Even in Bohr's theory of spectral series the same difficulty is felt. But in his theory the bold step is taken of adopting as a basic principle in dealing with the emission of radiation a relation between amounts of energy involving a linear relation between frequencies.

Bohr's theory of the origin of spectra is based on two fundamental assumptions:—

(1) An atomic system with an electron moving in a *stationary* orbit is associated with a definite amount of energy which can be calculated by employing the quantum principles in connexion with the laws of ordinary dynamics.

(2) When the atom passes from one stationary state to another, or the electron changes from one stationary orbit to another, there is an emission of *monochromatic* radiation of frequency  $\nu_r$  determined by the relation

$$h\nu_r = W' - W, \quad . \quad . \quad . \quad . \quad . \quad (5.1)$$

where  $W$  corresponds to the initial,  $W'$  to the final state of the system.

"Needless to say the founder of the new theory and his followers do not attempt to describe the mechanism of such an extraordinary performance, one, that is, that enables the atomic system to hit precisely upon the frequency  $\nu_r$  required by the assumption"\*.

The *kinematical* significance of Bohr's equation may be realized by expressing  $W$  in the form  $\frac{1}{2}nh\nu$ . The frequency of the radiation emitted is then given by

$$h\nu_r = \frac{1}{2}n'h\nu' - \frac{1}{2}nh\nu. \quad . \quad . \quad . \quad . \quad . \quad (5.2)$$

My object is to show that this relation can be interpreted by taking the frequency of the emitted radiation as identical with a definite frequency associated with a quantum tube or tubes of magnetic induction, such frequency being one characteristic feature of the system, both in its initial and in its final state.

In Part I. of this paper it has been shown that the integer  $n$  in the expression  $W = \frac{1}{2}nh\nu$  may be interpreted as the total number of quantum tubes linked with the orbit of the electron, whether the orbit be a circle or an ellipse. Consequently, when, in Bohr's theory, a change takes place from one stationary state to another and  $n$  changes to  $n'$ , there is an integral change in the total number of tubes linked with

\* Silberstein, 'Report on the Quantum Theory of Spectra,' p. 6 (1920).



the orbit. When radiation is *emitted* there is a *diminution* in the number of these tubes equal to  $n-n'$ . But it is assumed in the theory that, whatever may be the value of  $n-n'$ , only one quantum of radiation is emitted. On the view now suggested it is natural to suppose that the radiated energy is the energy associated with a single quantum tube, the emission of radiation being a process consisting in, or consequent upon, the liberation of one quantum tube from the atomic system. It is, however, only when the electron passes between neighbouring orbits that the diminution in the number of tubes,  $n-n'$ , is equal to unity. In general, the decrease in the number of tubes linked with the orbit is more than sufficient to account for the single tube we have supposed separated from the system. If, then, we regard magnetic tubes as entities which can change in form, but cannot be created or destroyed\* (so long, at least, as they are associated with an atomic system), we are forced to the conclusion that there must be some part of the system which can serve as a receptacle for the surplus tubes. Such a receptacle may be described as a "magneton," using that term in the wide sense I have advocated elsewhere† to denote that structure within the atom which may be regarded as the origin of the quantum magnetic tubes. We may employ the term without limiting ourselves to any precise model of the mechanism involved. It will cover the particular structure suggested by the term "ring electron," the more general case of the magneton of McLaren, or the "magnetic wheel" of E. T. Whittaker.

Consider the case of an atom consisting of a positive core and a negative electron. There are two possibilities presenting themselves. The core of the atom may be a magneton, as I have suggested in a previous paper on "An Atomic Model with a Magnetic Core"‡, or the negative electron may be a magneton§.

Without entering into a discussion of these alternatives, it will be sufficient for our present purpose to assume that the magneton is closely associated with an integral number

\* For an interesting discussion of the process of magnetization regarded as the opening out of molecular magnetic loops *which are already in existence*, and of the characteristics of such magnetic tubes of force, see Sir Oliver Lodge's lecture on "Magnetism and the Ether" (Journal of the Röntgen Society, xviii, July 1922).

† H. S. Allen, Proc. Roy. Soc. Edin. xlii. p. 213 (1922).

‡ H. S. Allen, Phil. Mag. xxix. p. 714 (1915). See also a paper by Th. Wereide, *Ann. d. Physik*, xlix. p. 966 (1916).

§ "The Case for a Ring Electron," Physical Society of London, Proceedings, xxxi. p. 49 (1919).

of quantum tubes of frequency  $\nu_r$ . As in Bohr's theory the electron is supposed to describe an orbit about the nucleus, the size of the orbit and the frequency being determined by the usual quantum relations. For simplicity we shall consider the case of a massive nucleus, which may be regarded as at rest.

Let  $n$  denote the number of quantum tubes linked with the orbit and also passing through the magneton, and  $n_r$  the number of quantum tubes associated with the magneton which are not linked with the orbit.

Then, in accordance with the principles discussed in the earlier portion of this paper, the electrokinetic energy of the system in its initial state is given by

$$T = \frac{1}{2}n_r h\nu_r + \frac{1}{2}nh(\nu + \nu_r). \quad (5.3)$$

Denoting the corresponding quantities in the final state by accented letters, we have, similarly,

$$T' = \frac{1}{2}n_r' h\nu_r' + \frac{1}{2}n'h(\nu' + \nu_r'). \quad (5.4)$$

To proceed further we have to make some specific assumptions with regard to the frequencies. In the first place, we assume that the frequency  $\nu_r$  remains unchanged in passing from the initial to the final state, and we identify this frequency with that of the emitted radiation.

In systems which emit hydrogen-like spectra the kinetic energy is numerically the same as Bohr's  $W$ . In his theory the kinetic energy in the new orbit is greater than that in the old, but the amount of potential energy set free is exactly twice the change in the kinetic energy. Consequently, an amount of energy is available for radiation which is equal to the change in the kinetic energy. This is

$$T' - T = \frac{1}{2}[(n_r' + n') - (n_r + n)]h\nu_r + \frac{1}{2}n'h\nu' - \frac{1}{2}nh\nu. \quad (5.5)$$

We now assume that in the change from one state to the other *one* quantum tube has been liberated from the magneton, and put

$$\frac{1}{2}h\nu_r = T' - T. \quad (5.6)$$

Hence

$$\frac{1}{2}h\nu_r = \frac{1}{2}[(n_r' + n') - (n_r + n)]h\nu_r + \frac{1}{2}n'h\nu' - \frac{1}{2}nh\nu. \quad (5.7)$$

But if a single quantum tube is liberated, the total number of bound tubes in the initial state is one greater than the total number in the final state, *i. e.*,

$$n_r + n = n_r' + n' + 1. \quad (5.8)$$

Thus the above equation reduces to

$$h\nu_r = \frac{1}{2}n'h\nu' - \frac{1}{2}nh\nu, \quad (5.9)$$

which is identical with that employed by Bohr.

It should be observed that in this theory the electron may be regarded as forming one member of a coupled system, and with each "bound" electron at least two frequencies are associated. The first of these,  $\nu_r$ , has been assumed the same in the initial and final state of the system, and identical with the frequency of the emitted radiation. The second frequency,  $\nu$ , is that on which the "binding" of the electron to the rest of the atom depends. Thus the frequency  $\nu_r$  corresponds to that met with in the classical electromagnetic theory of absorption and dispersion, whilst the frequency  $\nu$  is identical with that found in the theory of Bohr and Sommerfeld. Whilst in one sense it is not possible to "reconcile" the quantum theory with orthodox dynamics, the suggestions now put forward serve to indicate the possibility of a connexion between the two points of view, and even to show the general nature of the relationship.

It may be objected that the foregoing presentation implies that as the frequency of the monochromatic radiation is identified with the frequency of the magneton, that frequency is predetermined and there must be as many different atoms as there are lines in a spectral series. This objection carried more weight with me in 1921 than it does at the present time, because Prof. Whittaker has shown clearly by means of his quantum mechanism (1922) how frequency may be varied in an atomic model, whilst the number of magnetic tubes remains constant. In the present case, we may suppose that the frequency of the magneton itself may assume any value, but the catastrophic emission of radiation will occur when, and only when, the frequency assumes the particular value required by Bohr's equation.

## 6. SUMMARY AND CONCLUSION.

In earlier papers the hypothesis, first suggested by A. L. Bernoulli\*, of the existence of discrete tubes of magnetic induction determined by the ratio of Planck's constant  $h$  to the charge  $e$  of an electron, has been applied to the case of an electron moving in a circular or an elliptic orbit. In this paper more complex distributions are considered. Two magnetons or two electron orbits may be represented by two current circuits carrying currents  $i_1$  and  $i_2$ . The quantum conditions applied to this case are most simply interpreted by the same hypothesis of the

\* Bernoulli, *Archives des Sciences*, xlii., p. 24 (1916).

atomicity of magnetic tubes. The electrokinetic energy of a quantum tube is given by  $\frac{h}{8\pi e} \Sigma H ds$ . When the tube is linked with two current circuits,  $\Sigma H ds = 4\pi(i_1 + i_2)$ , assuming the tube passes through each circuit in the positive direction. Thus the electrokinetic energy associated with the tube is  $\frac{1}{2} \frac{h}{e} (i_1 + i_2)$ . When each circuit is equivalent to a single electron revolving in an orbit with assigned frequency ( $\nu_1$  or  $\nu_2$ ), this reduces to  $\frac{1}{2} h(\nu_1 + \nu_2)$ , or we may write it  $\frac{1}{2} h\nu$ , where  $\nu$  is a frequency characteristic of the tube under consideration. It is tempting to suppose that the frequency  $\nu$  appropriate to a particular tube corresponds to the frequency of a state of spin or vorticity associated with that tube. But the question as to whether such vorticity represents the actual physical state of the tube need not at present be discussed.

Incidentally, a mechanical model is described, which gives a very close representation of the electrical system of two current circuits.

The quantum relations are applied to the general case of any number of current circuits, and it is shown that there is no difficulty in generalising the previous results. It is pointed out that in this mode of formulating the energy of a system, frequency plays the part of an additive quantity. As this is a characteristic feature of Bohr's theory of spectral series, an attempt is made to apply the result to the interpretation of Bohr's theory. It is shown that Bohr's frequency relation

$$h\nu_r = \frac{1}{2} n' h\nu' - \frac{1}{2} n h\nu$$

can be interpreted by taking the frequency  $\nu_r$  of the emitted radiation as identical with that of a quantum tube or tubes, such frequency being characteristic of the system both in its initial and in its final state. Although the suggestions put forward do not abolish the conflict between the quantum theory and classical dynamics, they may serve to show more clearly the points of contact between the two theories. It may at least be said that a further step has been taken in the magnetic interpretation of the quantum.

University of St. Andrews,  
June 7, 1924.

XLVII. *Gas Ion Mobilities and their Independence of the Nature of the Ion.* By LEONARD B. LOEB\*.

SINCE 1916 the writer (1) has at various times attempted by means of crucial experiments to distinguish between the so-called classical theory of the "cluster ion" in gaseous ionization phenomena and the "small ion" theory of Sutherland (2) and Wellisch (3). In all cases these supposed crucial experiments gave results that were, while suggestive of a small ion interpretation, never decisively in favour of either theory. In 1917 (4) the writer summarized the field as a whole, and showed that as regards most of the ion phenomena the explanations on either theory were equally good. A knowledge of the nature of the ion is of value as it may throw considerable light on the law of forces acting between molecules and charges, and as it may have some bearing on the interpretation of ionization phenomena in solutions.

In a recent (5), but futile, attempt to distinguish between the two theories based on measuring the mobilities of ions in mixtures of dry ammonia gas and air, the writer found that the mobilities of the ions varied inversely as the square root of the product of the molecular weight of the gas into the dielectric constant of the gas diminished by unity. Such a variation of mobility with the dielectric constant of the gas does not agree with Wellisch's (3) equation for the mobility of a small ion, in which the mobility varies inversely as the first power of a term of the form  $(1 + b(D - 1))$ , where  $b$  is a constant. By introducing a term for the shortening of the mean free path assuming a cluster ion (whose size could be estimated according to a theory of Langevin (7) based on an inverse fifth power law of force) into the mobility equation of Langevin (6) for a cluster ion in a somewhat questionable way, the writer obtained an equation in which the mobility varied approximately inversely as the square root of the dielectric constant diminished by unity.

Recently Sir J. J. Thomson (8) has published a theoretical treatment of the question of the change of the mean free path of an ion in virtue of the forces it exerts on neutral molecules. This treatment is quite rigorous and is based on the assumption of an inverse fifth power law of force (that is, such a law of force as a charged body would exert on a neutral dielectric body of a dielectric constant  $D$ ). Thomson also shows how the resulting equation must be modified in

\* Communicated by the Author.

case an inverse cube law of force had been assumed (that is, in case one assumed that the attraction of the ion was that of a charged body on a molecular dipole). It can be shown that if this shortening of the mean free path computed by Thomson on an inverse fifth power law be introduced into the Langevin (6) equation for ionic mobilities, and if the shortening be ascribed to the force of attraction of an ionic charge on a gas molecule whose dielectric constant in bulk is  $D$ , the mobility will vary inversely as the square root of the product of the mass of the gas molecules into the dielectric constant diminished by unity, as found by experiment.

On introducing the factor for shortening the mean free path of an ion due to the charge, mentioned above, into the Langevin (6, 9) mobility equation which in its method of derivation is consistent with the Thomson theory, certain very interesting transformations of the equation for the mobility of the ions occur. The transformations are such that they not only practically completely eliminate any factor involving a specific hypothesis of the nature of the ion from the equation, thus making it impossible from mobility measurements to decide upon the nature of the ions: but furthermore, the resulting equation so completely predicts qualitatively, and even quantitatively, most of the characteristic phenomena exhibited by ions that it merits a fuller discussion. It will be the purpose of this paper to set forth briefly the various phenomena to be explained by any theory of ionic mobility and the manner in which this theory explains them.

For a charged particle of mass  $m$  moving in a gas whose molecules have a mass  $M$ , with a relative velocity  $V$ , J. J. Thomson (8) finds that the mean free path of the charged particle is to that of the uncharged molecule as

$$\frac{\lambda'}{\lambda} = \frac{1}{2.2 \left( \frac{2k}{\sigma^4 \frac{Mm}{M+m} V^2} \right)^{\frac{1}{2}}}.$$

Here  $k$  is the force constant of the attraction between the ion and the molecule. At present it is hard to be sure of the exact value of this force constant. But one might assume, as Langevin (7) has done, that the molecules act like dielectric bodies such that in the field produced by an ion they are acted on by a force

$$F = \frac{(D-1)e^2}{2\pi n_0 r^5}.$$

Here  $D$  is the dielectric constant of the gas in bulk;  $n_0$  is

2 H 2

the number of molecules per c.c. under the conditions pertaining to the measurement of  $D$ ;  $e$  is the electron; and  $r$  is the distance of the centre of the ion from that of the

molecule. Thus  $k$  becomes  $\frac{(D-1)e^2}{2\pi n_0}$ . In the equation of

Thomson, the quantity  $\sigma$  is the sum of the radii of the ion and the molecule and corresponds to the average distance of approach on impact.  $V$  is the relative velocity of approach

of the ion and molecule, and the quantity  $\frac{mM}{M+m} V^2$  is for

the present purposes none other than twice the kinetic energy of agitation of the gas molecules at the temperature of the gas, from the definition of this quantity as used by Thomson. It may consequently be replaced by  $Mc^2$  in the equation. Thus one can write :

$$\lambda' = \frac{\lambda}{2 \cdot 2 \left\{ \frac{2(D-1)e^2}{2\pi n_0 \sigma^4 Mc^2} \right\}^{\frac{1}{2}}}$$

where  $c$  is the square root of the average square speed.

Langevin (6, 9) deduced an equation for the mobility of a complex cluster ion of mass  $m$  among gas molecules of mass  $M$  on the basis of the kinetic theory of gases assuming no forces to act between the ions and the neutral molecules. This equation takes the form :

$$K = .815 \frac{e}{M} \frac{\lambda'}{c} \sqrt{\frac{M+m}{m}}.$$

Here  $\lambda'$  is the mean free path of the ion cluster. Since, as J. J. Thomson points out, his factor for the reduction of the mean free path of an ion due to its attractive forces is independent of an assumption of a cluster theory or not, one can introduce \* the Thomson factor for the shortening of the mean free path into Langevin's equation †.

\* This is subject to one restriction, however, and that is, that the Thomson factor, because of its derivation, cannot be used where it is less than unity.

† This may seem a questionable procedure, but short of a very complicated and tedious analysis and re-derivation of Langevin's equation introducing attractive forces into it, the matter cannot be treated rigorously. As the results seem to justify this procedure the fault committed is not as serious as it would be on a strictly theoretical basis.

The combined equations then take the form :

$$K = .815 \frac{e \lambda}{m c} \frac{\sqrt{M+m}}{2.2 \left\{ \frac{(D-1)e^2}{\pi n_0 \sigma^4 M c^2} \right\}^{\frac{1}{2}}}.$$

If now, the value for  $\lambda$  from the kinetic theory of gases, to

wit,  $\lambda = \frac{1}{\pi \sqrt{2n}\sigma^2}$  be placed in the combined equations, the equation reduces to the form :

$$K = \frac{.815}{2.2 \sqrt{2\pi}} \frac{\sqrt{M+m}}{n M^{\frac{1}{2}} (D-1)^{\frac{1}{2}} n_0^{\frac{1}{2}}}.$$

This can be still further simplified by replacing  $n$  the number of molecules per c.c. of the gas in which the ions are moving by  $n_0 (p/760)$ , where  $p$  is the pressure in mm. of mercury, by replacing  $M$  by  $M_0 \mu$  where  $\mu$  is the mass of an atom of hydrogen, and  $M_0$  is the molecular weight, and by writing that  $m = bM$ , so that the final form of the equation is :

$$K = \frac{.815}{2.2 \sqrt{2\pi} (\mu n_0^{\frac{1}{2}}) M_0^{\frac{1}{2}} (D-1)^{\frac{1}{2}}} \frac{\sqrt{M+m}}{m} \frac{p}{760}$$

or better :

$$K = \frac{A \sqrt{1+b}}{760 \sqrt{(D-1) M_0}},$$

where  $A$  is a constant depending on the Avogadro number, the mass of an atom of hydrogen, and a numerical coefficient.

This striking transformation of the ion mobility equation is now capable of verification on the basis of its ability to predict the properties of the gas ions. This will be done in what follows.

### I. Mobility and the Size and Mass of the Ion.

It is seen at once that the equation for the mobility of the ion is independent of both the size and the mass of the ion

except for the small factor  $\sqrt{\frac{1+b}{b}}$ . This varies in value



from 1.42 for a single small ion ( $b=1$ ) to unity for a very large cluster for which  $b$  is great compared with unity.

1. It had long ago been shown by Franck (10) that the mobility of radioactive recoil atoms in hydrogen was about the same as that of normal ions in hydrogen, although their mass was considerably above that of the hydrogen molecules. Likewise Wellisch (11) had shown that the mobility of methyl iodide ions in hydrogen was the same as that of hydrogen ions in hydrogen in spite of their difference in mass. In neither of these experiments was the precision very high, and it is very doubtful whether the effect of the factor  $b$  in the equation above could have been detected in these experiments. Thus, their results are predicted by the new theory, a feat that no theory heretofore has succeeded in doing without further assumptions.

2. The values of the mobility of gas ions seems to be completely independent of any factor related to the diameter of the ions or the gas molecules. The writer had for a long time wondered at the failure to obtain any correlation of mobility with molecular or ionic diameters, although this factor appears in all mobility equations, and although it varies very widely from gas to gas. The new theory leads one to expect this independence.

3. The equation also shows that from the ionic mobilities alone, except for the small variation due to  $b$ , *it should be impossible to determine the nature of the ion from any mobility experiments*. It is for this reason that the previous attempts to distinguish between the cluster and small ion theories on the basis of crucial experiments on the part of the writer and other workers have always yielded indecisive results. Thus, the writer (1) and Professor Yen (12) attempted to distinguish between the theories by measuring mobilities in very high electric fields, where owing to their high kinetic energies the cluster ions should have broken up. The experiments showed no change in mobility, while on a cluster theory the mobility should have increased about fourfold, and on a small ion theory it should have decreased by a factor of about 0.4.

4. The small change of mobility for a change in mass of the cluster represented by the factor containing  $b$  should, however, on careful measurement, become manifest every time the ion permanently changes its size. It is perhaps on the basis of such a change that the reduction of the mobility of the positive ions in nitrogen, hydrogen, and air, with age, discovered by Erikson (13) and confirmed by Wahlén (14), as well as the difference in mobility of +

and — ions, may be explained. If one assumes that the negative ion is a single charged molecule carrying an extra electron and on formation the positive ion is likewise a molecule that has lost an electron, but that with age the *positive ion* adds a cluster of five molecules around it, then its initial mobility which equals the negative will, when it has added its five molecules, be reduced from 1.8 cm./sec., which it has as a new ion, to 1.4 cm./sec. This corresponds

to a change in the value of  $\sqrt{\frac{1+b}{b}}$  from 1.42 to 1.09, which takes place for a change in  $b$  of from 1 to 5.

If the mass of the ion became very small, as for example in the case of an electron in a gas, the present theory would hardly be applicable. For in that case the electron picks up energy from the field, making the factor of J. J. Thomson approach unity, so that the shortening of the mean free path ceases to count and the equations of K. T. Compton (15) may be applied.

## II. *The Mobilities of the Ions and Pressure.*

The mobility of positive ions has been shown to vary inversely with pressure for pressures ranging from a few tenths of a millimetre to close to 100 atmospheres (16, 17). The same holds true for the negative ions at higher pressures; and, as shown by Wellisch (18) and confirmed by Loeb (19), for the lower pressures, *provided the electrons are given time to attach to molecules to form ions before they enter the measuring field*. Otherwise ionic mobilities are not measured, the mobilities obtained corresponding to carriers part ion and part electron of very widely different mobilities (28, 29). At the higher pressure ranges, above 66 atmospheres, the mobilities decrease a little less rapidly than the inverse pressure law would demand according to McLennan (17). The significance of this effect is completely obscure at present, and it is too small an effect in any case to merit a longer discussion at this point. As is seen, the general behaviour is predicted by the equation through the factor  $p/760$  in the denominator.

## III. *The Mobility and the Mass of the Gas Molecules in which the Ion moves.*

Long ago, Kaufmann (20) stated that for the more "permanent gases," the mobility varied inversely as the square root of the molecular weight of the gas in which the ion moved. This rule, known as Kaufmann's rule, was extended

by Loeb (4) to the case of all gases and vapours provided a correction factor involving the dielectric constant of the gas was applied. It had been predicted by the older ionic mobility equations, such as the Langevin equation, since the factor  $c$  of that equation varies as the square root of  $M$ . In order to make the equation hold, however, it became necessary to assume that  $K$  was independent of all factors other than mass and dielectric constant, as one went from gas to gas. This seemed absurd in view of the fact that the equations also contained the factor  $\lambda$ . As is seen, the present theory predicts that outside of a variation with  $D$  and  $p$ , the mobility should only vary inversely as the square root of  $M$ .

#### IV. *The Mobility and Temperature.*

All previous theories of ionic mobilities had predicted that as the mobility varied inversely as  $c$  it should vary inversely as the absolute temperature of the gas. Although the results of different mobility measurements do not completely agree as to the exact amount of variation of mobility with temperature, all the observers agree in finding *very little change with temperature*. Sutherland (21), in analogy with his treatment of the disagreement of the observed and predicted variation of gaseous viscosity with the temperature, derived an equation giving the change in ionic mobility with temperature. The theory fitted the observed results of Phillips (22) quite well. Erikson (23), in some very careful work at constant density, found that the mobility was independent of temperature down to nearly liquid air temperatures, where the mobility showed a decrease of about 10 per cent. The present theory leads one to expect that  $K$  will be independent of temperature. This agrees better with the experimental facts than any other theory. At the lowest temperatures the mobilities and their variations need further study and measurement.

The same reasoning would explain why it was that the writer (1) and Professor Yen (12) failed to find the expected decrease in mobility of the ions in high electrical fields, which, as was stated above, should have been a reduction by a factor of 0.4. A decrease of this sort was expected because owing to the high fields the average velocity of the ion was about 2.5 times the velocity of thermal agitation of the gas molecules. In such a case, with the combined Thomson and Langevin equations, the factors  $c$  become the

velocities of the ions and cancel out as they do in the case of ions in temperature equilibrium with the gas. Thus the new equation applies to this case and we see why the experiment yielded an indecisive result.

#### V. Mobilities and the Dielectric Constant of the Gas.

It had been pointed out in 1917 (4) that the ionic mobilities varied from gas to gas inversely as a product of the fourth root of the dielectric constant of the gas diminished by unity, multiplied by the square root of the molecular weight. This relationship, independent of any theoretical foundation, seemed to hold fairly well even with the large variations of the sources from which the data came. Recently the writer (5) has shown that for a set of measurements made under identical conditions in mixtures of  $\text{NH}_3$  gas and air the mobility varied much more closely according to the inverse square root of the average dielectric constant of the mixture diminished by unity. The suggested combined equations of Thomson and Langevin lead to a variation in agreement with the later measurements. This variation is distinctly different from the variation with the inverse fourth root of  $D-1$ , and would cause a poorer agreement in a table such as reproduced in the earlier (4) paper than there was found originally. It must be pointed out that the table there given is based on the very diverse results of mobility measurements by different observers using different methods. Thus, the values are not consistent and it is not surprising that the agreement is not good. For example, the value for  $K$  in air was formerly taken as 1.4 relative to the value .74 for  $\text{NH}_3$ . The recent measurements made under identical conditions in both cases give the relative values of  $K$  as 1.6 for air against .52 for  $\text{NH}_3$ . This result is much more consistent with the Langevin-Thomson theory than with the empirical rule previously laid down. Before one can accept the new theory as established in this regard, one must, however, be able to extend the ammonia-air measurements to a number of other gases.

In gases which have a markedly polar nature, *i. e.* those that have permanent electrical moments of their own, such as  $\text{HCl}$ , the force acting should be the inverse third power law. Such a law, according to J. J. Thomson, should have the force factor  $k$  (*i. e.*  $D-1$ ) acting in the denominator in the first power. It would be of considerable importance to test this out experimentally, and such experiments are now being undertaken.

VI. *Electron Attachment and the Theory.*

The writer (24) has shown that in its broad aspects the theory of negative ion formation proposed by J. J. Thomson (24) is able to predict the observed phenomena of attachment of electrons to molecules of gases quite successfully. This theory assumes that the electron does not attach to the molecule on its first impact, but that it does so in general after  $n$  impacts with molecules, where  $n$  is a constant depending on the chemical nature of the gas only. This idea is elaborated further by J. J. Thomson (25) in the recent paper in which the theory of the change of the mean free path for charged molecules is discussed. He shows that it follows naturally from the considerations such as lie at the basis of the theory proposed, and that the predicted value of  $n$  for air is of the same order of magnitude as the observed. This theory would make it appear that the electrons did not attach unless their energy were low and would lead one to expect a variation with the nature of the molecules as is observed. It might be pointed out that Bailey (26) recently also suggested that the attachment was limited to electrons of low velocity.

It seems to the writer, however, that the type of theory as applied by J. J. Thomson to the treatment of the combination of electrons and molecules would be less likely to hold on the modern theory of atomic structure, than it would for the junction of ions and molecules. It seems likely that on the Bohr theory the electron would not attach to a molecule to make a negative ion unless it struck the molecule in such a manner and under energy conditions such that it could assume a stable orbit about the molecule consistent with the rest of the molecule's electronic system. It is significant that the molecular types noted for the stability of their electronic system (*e.g.*, as suggested by G. N. Lewis, 27) are those that apparently never attach an electron at all. It is further very certain from measurements that the electron once attached does not leave the molecule again. This points to a very stable union. It also seems possible from the experiments of Erikson (13) and Wahlin (14) that the positive ions consist of very stable aggregates of molecules, about a molecule rendered unstable by itself through the loss of an electron. In any case, the proposed theory is in no way inconsistent with the attachment results, while the possibility of the formation of more stable aggregates must be considered.

## VII. Ions and Condensation.

As was pointed out in 1917 (4), the condensation of super-saturated vapours on ions is in no way essentially connected with any theory of ionic behaviour. All that is needed is that an unstable droplet that would evaporate under given conditions of supersaturation should pick up an ion, as do Millikan's oil drops, in order to grow to a visible size as indicated by the theory of J. J. Thomson (30).

*Evaluations of Gas Ion Mobilities from the New Theory.*

Numerically, the mobilities of the ions may be computed for any gas from the equation deduced, by taking the values of  $M_0$  and  $D$  from tables, evaluating the constant  $A$ , and assuming a value of  $b$ . If the resulting quantity be divided by 300, the mobility is given in cm./sec. per volt./cm. A table of values computed for a number of gases follows, assuming  $b=1$ . It must be noted that the observed values are some of them very old values, and that they represent measurements made in diverse manners. The values of  $K$  in the vapours of the less volatile substances are most likely to be in error since here the technique of measurement is not so simple.

Gas.	$M_0$ .	$D-1$ .	$(D-1) M_0$ .	K computed. K observed.	
				$\frac{1.04 \times 10^{-1}}{\sqrt{(D-1)M_0}}$	
H <sub>2</sub> .....	2	$2.73 \times 10^{-4}$	$2.34 \times 10^{-2}$	4.43	6.02
He .....	4	$0.74 \times 10^{-4}$	$1.72 \times 10^{-2}$	6.02	5.09
A .....	40	$1.0 \times 10^{-4}$	$6.33 \times 10^{-2}$	1.64	1.37
Air .....	28.8	$5.9 \times 10^{-4}$	$13.1 \times 10^{-2}$	0.79	1.35-1.6*
NH <sub>3</sub> .....	17	$77.0 \times 10^{-4}$	$36.2 \times 10^{-2}$	0.29	0.74-1.52*
CO <sub>2</sub> .....	44	$9.6 \times 10^{-4}$	$20.6 \times 10^{-2}$	0.51	0.81
CO .....	28	$6.9 \times 10^{-4}$	$14.0 \times 10^{-2}$	0.74	1.10
SO <sub>2</sub> .....	64	$90.5 \times 10^{-4}$	$76.2 \times 10^{-2}$	0.14	0.44
N <sub>2</sub> O .....	44	$10.7 \times 10^{-4}$	$21.8 \times 10^{-2}$	0.48	0.82
C <sub>2</sub> H <sub>5</sub> OH ...	46	$94.0 \times 10^{-4}$	$66.0 \times 10^{-2}$	0.16	0.34
CCl <sub>4</sub> .....	154	$42.0 \times 10^{-4}$	$80.5 \times 10^{-2}$	0.13	0.30
C <sub>2</sub> H <sub>5</sub> Cl .....	65.5	$155.0 \times 10^{-4}$	$101.0 \times 10^{-2}$	0.10	0.33
C <sub>4</sub> H <sub>10</sub> O .....	74.0	$74.2 \times 10^{-4}$	$74.2 \times 10^{-2}$	0.14	0.24

\* These values recently measured under the same conditions by writer.

It can be seen that the mobilities computed are of the right order of magnitude and do not differ widely from the observed values in some cases. In the vapours of high dielectric constant the deviation between observed and computed values is the greatest. Notwithstanding these deviations, the evaluation of the ionic mobility from such apparently unexpected quantities, which are independent of mean free path and charge, and which fit the experimental values better than any other ion theory, must impress one with the plausibility of the theory underlying it.

### VIII. *Conclusions.*

From the foregoing, one may safely conclude that the combined Thomson-Langevin equations as presented furnish us with a theory of ionic behaviour that predicts better than any single theory heretofore proposed the behaviour of the gas ions under various conditions. It is further seen that the

theory shows that except for the effect of the factor  $\sqrt{\frac{1+b}{b}}$

there is no quantity in the mobility equation which permits one to decide on the nature of the ion. Thus, except for this feature, all attempts to distinguish between a cluster and a small ion theory on the basis of mobility measurements are futile.

While the theory is applicable to either type of ion theory, as J. J. Thomson points out, the assumption of an inverse fifth power law leads to the use of the term

$$2 \cdot 2 \left( \frac{2k}{\sigma^4 \frac{Mm}{M+m} V^2} \right)^{\frac{1}{2}}$$

for the shortening of the mean free path which must be less than unity in order that the mean free path begin to be decreased. This means that when

$$2 \cdot 2 \left( \frac{2k}{\sigma^4 \frac{Mm}{M+m} V^2} \right)^{\frac{1}{2}}$$

becomes greater than unity the value of the potential energy of the molecule at a distance  $\sigma$  from the ion  $\left( \frac{k}{4\sigma^4} \right)$  is greater than the kinetic energy of agitation of the molecules and ions,  $\left( \frac{1}{2} \frac{Mm}{M+m} V^2 \right)$ . Such a relation is also the condition for

a cluster formation. Thus, as J. J. Thomson shows later in his paper, the ion on the average forms a cluster and dissociates it again all along its paths. This formation and dissociation forms a labile cluster which one is unconscious of as far as the mobility measurements are concerned. Thus, the mobility of the ion is not just that of a single charged molecule, but varies from it by the quantity depending on the value of  $b$ . The variation is small. Since, owing to the statistical nature of the cluster formation, some ions have more than their share of clustering during a measurement

while others have less, the factor  $\sqrt{\frac{1+b}{b}}$  should cause a

slight variation of  $K$  about the mean value of  $K$  for the ions. This would produce asymptotic portions to the curves obtained in determining ionic mobilities in experimental measurement. Such asymptotic feet have always been observed, but since such feet could also be caused by instrumental irregularities it becomes impossible to test the theory on this basis. To explain the Erikson-Wahlin (13) (14) effect, it becomes further essential to this theory to assume that under some circumstances the clustering may take a more permanent form than suggested by Thomson. That this should occur for a molecule that is rendered unstable through the loss of an electron would not be surprising.

Thus the theory of Thomson, when combined with the theory of Langevin, clears up much that is obscure in the behaviour of gas ions, puts an end to the futile cluster-small ion theory controversy, tells what law of force is exerted by the ion on the majority of gas molecules, and yields an adequate theoretical background to guide the future workers in the field.

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May 18, 1924.

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#### XLVIII. *On the Escape of Heat from the Earth's Crust.*

*By J. R. COTTER, M.A.\**

**I**N two recently-published papers (*Phil. Mag.* Ser. 6, vol. xlv. No. 270, June 1923, and vol. xlv. No. 271, July 1923) Prof. Joly has given an account of his theory of the causes which produce the great geological revolutions. The present paper is an attempt to determine mathematically the temperature changes which occur in the sub-oceanic parts of the earth's crust after the close of a revolution. The preliminary sketch of the processes which are assumed to take place is based partly on the papers above referred to, and partly on an explanation of the theory verbally communicated by Prof. Joly, who has also supplied me with all the numerical data which are here made use of.

According to Prof. Joly's theory, that portion of the earth's crust immediately beneath the ocean-floor consists of basalt, in which a continual generation of heat takes place, owing to the presence of radioactive materials. Prof. Joly concludes on experimental grounds that the heavier ultra-basic materials which probably underlie this stratum of basalt are much less radioactive. For the purpose of simplifying the investigation, I shall assume that no transmission of heat

\* Communicated by the Author.

occurs through that horizon which may be regarded as the lower boundary of the basalt. The modifications which would have to be made in the theory when the radioactivity of the underlying rock is taken into account need not here be considered. The temperature of the upper surface of the basalt will be taken to be  $0^{\circ}\text{C}$ ., which is approximately the temperature of the ocean-floor.

Let us suppose that at some stage in the history of the earth's crust the basalt is solid throughout. As we descend from the upper surface, the temperature will rise until at a certain depth the melting-point of basalt is reached. If we denote the melting-point by  $\theta_0$ , then we may call this horizon the  $\theta_0$  geotherm. Below this level the rock is supposed to be everywhere at its melting-point. The temperature will not be quite uniform, but will increase slowly with depth, since the melting-point of basalt rises with increasing pressure. A long period of quiescence will ensue, during which the radioactive heat generated above the  $\theta_0$  geotherm will escape by conduction through the ocean-floor, while below this geotherm the heat generated will become latent owing to liquefaction of the rock, the temperature remaining steady all the time. It seems probable that the material in this lower portion would preserve its rigidity till an advanced stage of liquefaction has been reached, being in a condition somewhat resembling that of a sponge filled with water. A period of activity would now set in, starting with the breakdown of the weakened material owing to the disruptive action of tidal forces. Circulation might begin slowly, but would rapidly increase, because the descending portions would tend to solidify owing to increase of pressure, so that the increase of density due to solidification would accelerate the rate of descent; while the ascending portions would become more fully liquefied and would rise faster. As soon as circulation became general, a precipitate of solid material would begin to be formed at the bottom of the liquid mass; while at the same time the rest of the medium, up to the  $\theta_0$  geotherm, would become quite fluid, its temperature being nearly uniform and equal to the temperature of the solid deposit—that is, the temperature of the melting-point of basalt at a pressure equal to that of the fluid at its lowest level. Thus the upper part of the fluid would be above the melting-point appropriate to its pressure, and it would begin to melt away and erode the solid rock above it—that is, it would push the  $\theta_0$  geotherm upward. This process would be comparatively rapid at first, but would fall off owing to two causes: first, because as the fluid became

shallower owing to the deposit of solid, its temperature would fall, and secondly, because the loss of heat by conduction through the ocean-floor would become accelerated as the geotherms rose. Prof. Joly thinks that the  $\theta_0$  geotherm would rise to within a very few miles of the surface. It would, however, finally become stationary and then descend. At this stage the escape of heat would be very rapid, and the rate of solidification at the bottom would also be rapid. There seems little reason to doubt that the whole would eventually become solid again, and cooling would go on till it recovered its initial condition and initial distribution of temperature. The whole series of changes would form a cycle, which would be repeated.

It would not be easy to determine the rate at which the  $\theta_0$  geotherm would rise, but an approximate estimation of the rate at which it would fall can be made, and this is the object of the present paper.

In the first place, it is necessary to observe that there is a maximum depth, below which this isotherm cannot fall. This depth, which will be denoted by the letter  $l$ , is such that it is just possible for all the heat generated by radioactive agency to pass upward by conduction when no access of heat takes place from below. This depth, as calculated below, is about 30.6 miles. Neglecting, for the sake of simplicity, the variation of the melting-point of basalt with pressure, we may take this melting-point  $\theta_0$  to be a constant and equal to  $1150^\circ\text{C}$ . This assumption implies that no conduction of heat takes place below the  $\theta_0$  geotherm. If we represent distance measured vertically downward from the ocean-floor by  $x$ , then we may confine our attention to the stratum between the two horizontal planes  $x=0$  and  $x=l$ , the former being kept at zero temperature, and the latter being regarded as a boundary impervious to heat. Since we do not know the initial position of the  $\theta_0$  geotherm, it will be convenient to assume that it starts from the ocean-floor. It will be seen that this assumption can make little difference in the time estimate, as the initial cooling would be very rapid.

We have now a perfectly definite mathematical problem to solve. Given a uniformly radioactive medium bounded by the parallel planes  $x=0$  and  $x=l$ , it is required to find the distribution of temperature at any time  $t$ , the upper surface being maintained at zero temperature and the lower being impervious to heat, the whole being initially solid and at the temperature of the melting-point. We must know the radioactivity, conductivity, specific heat, and density.

For our purpose, the only difference between sensible heat and latent heat is that the latter is not conducted. It will therefore make no difference in the solution of the problem if we suppose that the substance does not melt, and that its temperature may rise above  $\theta_0$ , provided that we also make the assumption that the conductivity is zero everywhere below the  $\theta_0$  geotherm. Even in this form, the mathematical difficulties of the problem are so formidable that it does not seem possible to solve it. This is due to the fact that the plane which separates the upper conducting portion from the lower non-conducting part is a moving plane, the rate of movement of which has to be determined by the solution of the equations. In these circumstances I have been compelled to make the further assumption that the conductivity is uniform throughout. Some remarks will be made later on the nature of the error introduced by this assumption.

The simplified problem may now be stated as follows:— Given a medium whose radioactivity is such that the temperature in insulated material would rise  $a$  degrees per second, and whose diffusivity (Maxwell's thermometric conductivity) is  $\kappa$ , required to determine the temperature distribution at any time  $t$ , if the initial temperature is  $\theta_0$  throughout, and if the medium is contained within two fixed parallel planes  $x=0$  and  $x=l$ , of which the former is maintained at zero temperature, while the latter is impervious to heat.

The differential equation of conduction for a non-radioactive medium would be

$$\frac{\partial \theta}{\partial t} = \kappa \frac{\partial^2 \theta}{\partial x^2}.$$

If the medium is radioactive, the rate of rise of temperature  $\partial \theta / \partial t$  is increased by an amount  $a$ , so that the equation becomes

$$\frac{\partial \theta}{\partial t} = \kappa \frac{\partial^2 \theta}{\partial x^2} + a. \quad . \quad . \quad . \quad (1)$$

This equation reduces at once to the preceding form if we put  $\theta = v + at$ . The solution of this is well known. As written below, it is merely a special case of a more general solution which I have taken from H. S. Carslaw's 'Fourier's Series and Integrals,' § 103 (1st ed. 1906). The required solution is

$$\theta = \frac{a x (2l - x)}{2\kappa} + \frac{1}{\pi} \sum \frac{1}{n} \left( \theta_0 - \frac{4al^2}{n^2 \pi^2 \kappa} \right) e^{-\frac{n^2 \pi^2 \kappa t}{4l^2}} \sin \frac{n\pi x}{2l}, \quad (2)$$

where  $\theta$  is the temperature at the plane  $x$  and at time  $t$ .

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$\Sigma'$  here signifies the sum of an infinite series in which the values of  $n$  in successive terms are the odd integers 1, 3, 5, etc. It is easy to verify that this solution satisfies all the required conditions.

If  $l$  is the maximum depth to which the  $\theta_0$  geotherm can possibly descend, then  $\theta = \theta_0$  when  $x = l$ , and  $t$  is infinite. Substituting these values, we get

$$\theta_0 = \frac{al^2}{2\kappa}, \quad \dots \dots \dots (3)$$

and if we use this equation to eliminate  $\kappa$  from (2), it becomes

$$\frac{\theta}{\theta_0} = \frac{x}{l} \left( 2 - \frac{x}{l} \right) + \frac{4}{\pi} \Sigma' \frac{1}{n} \left( 1 - \frac{8}{n^2 \pi^2} \right) e^{-\frac{n^2 \pi^2 a t}{2\theta_0}} \sin \frac{n \pi x}{2l}. \quad (4)$$

The following are the data adopted by Prof. Joly :—

Melting-point of basalt =  $1150^\circ \text{C}$ .

Heat developed per sec. per gram =  $12.64 \times 10^{-14}$  cal.

Density of basalt = 3.0, sp. heat = 0.267.

Conductivity of basalt = 0.004.

From these figures we get  $\kappa = 0.005$  sq. cm. per sec., and  $a = 47.3 \times 10^{-14}$  degree C. per sec.

Substituting in (3), we get  $l = 30.6$  miles.

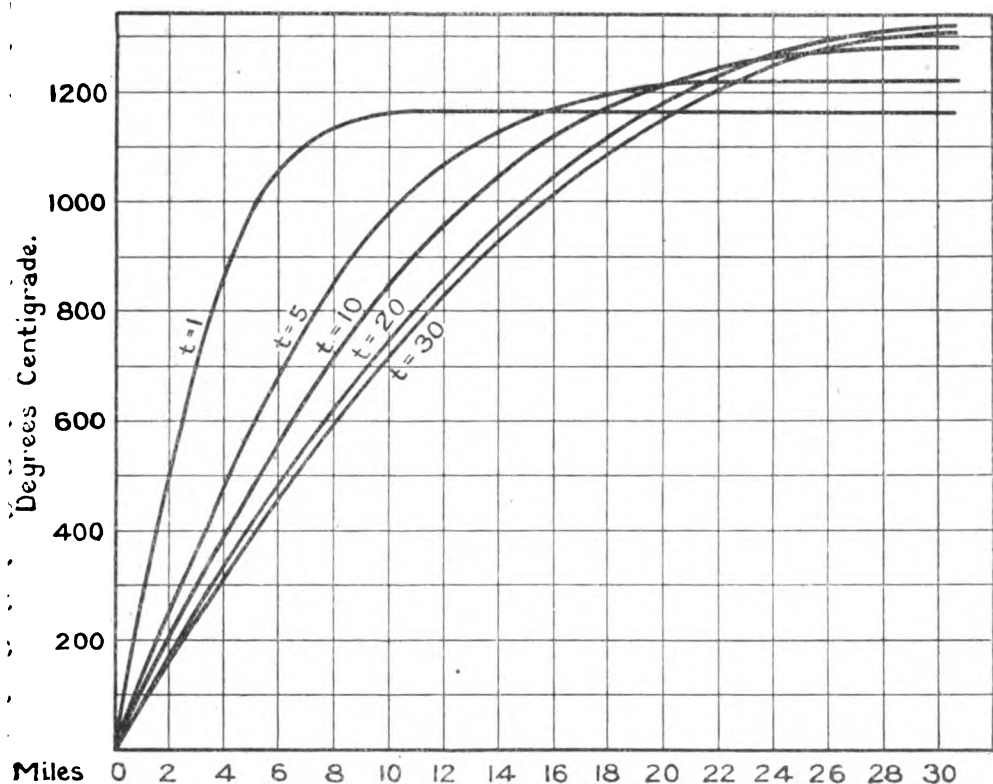
If, as will be convenient, we take one million years as our unit of time, then  $a = 14^\circ.9 \text{ C. per million years}$ . Using these values, the following figures for  $\theta$  have been calculated from (4) :—

Temperature  $\theta$  for different Times and Distances.

Time (millions of years).	Distance in miles from surface.					
	5.1	10.2	15.3	20.4	25.5	30.6
1 .. .. .	999.2	1160.9	1164.8	1164.9	1164.9	1164.9
5 .. .. .	611.6	999.9	1166.5	1214.3	1223.3	1224.4
10 .. .. .	492.0	864.8	1100.3	1222.5	1273.3	1286.2
15 .. .. .	444.7	799.5	1052.4	1210.5	1292.7	1317.6
20 .. .. .	421.2	764.5	1022.4	1196.5	1295.0	1326.5
25 .. .. .	408.1	743.9	1002.5	1183.2	1289.0	1323.8
30 .. .. .	400.0	730.6	988.0	1170.8	1279.6	1315.7

Since the rise of temperature in insulated material is  $14^\circ.9$  in a million years, it will be seen that the last 15 miles lose no heat in the first million years. Actually, the calculation shows a very slight fall, affecting the second decimal place only.

I have traced the curves of temperature distribution for  $t = 1, 5, 10, 20$ , and 30 million years. The diagram would be confusing if more curves were included.



The position of the  $1150^{\circ}$  geotherm was derived from the curves and then calculated independently. The following results were obtained :—

Depth of the  $1150^{\circ}$  Geotherm at different Times.

Time (millions of years).	1.	5.	10.	15.	20.	25.	30.
Depth (miles) .....	8.6	14.5	17.0	18.1	18.8	19.3	19.6

The error introduced by omitting to treat the portion of the medium above  $1150^{\circ}$  as non-conducting does not become appreciable until a considerable thickness has been cooled below that temperature. This is evident from the flatness of the curves  $t = 1$  and  $t = 5$  at their upper parts. It is clear

that actually the heat generated in the lower regions would be held back, instead of being partly conducted away, so that the geotherms would advance somewhat farther than is indicated by the above calculations. We may conclude that in 30 million years the  $1150^{\circ}$  isotherm would descend to a depth of at least 20 miles. Again, if in equation (2) we put  $l = 26.2$  miles instead of 30.6, we find that in 30 million years the  $1150^{\circ}$  geotherm would just reach to 26.2 miles. Here no heat is held back, and as the escape of heat is facilitated by conferring on any part of the medium a greater conductivity than it actually possesses, this result constitutes a major limit to the distance. Thus in 30 million years the  $1150^{\circ}$  geotherm attains a depth which is greater than 19.6 miles and less than 26.2 miles.

XLIX. *On the Discontinuous Flow of Liquid past a Wedge of Small Angle.* By W. B. MORTON, M.A., Queen's University, Belfast \*.

*Introduction and Summary.*

THIS paper is in continuation of one published in the Philosophical Magazine of May 1921†, in which was treated the flow of liquid past a wedge of any angle. It was suggested to me by Mr. T. C. Tobin that it would be of interest to examine specially the case in which the angle of the wedge and the angle at which its face is met by the stream are both small, since this may be regarded as a rough approximation to what happens in the case of a screw-propeller. It seemed possible that the rather intractable analysis of the former paper might be capable of simplification by way of an approximate solution when the angles are small. I have not made much progress in this direction with motion of the most general type, when the backward part of the stream-line along the front face, passing the angle of the wedge, bends round and is caught by the back face, enclosing a pocket of dead water (see fig. 2 of the former paper). In the two limiting cases, however, designated by the names of Kirchhoff and Bobyleff, I have found some simplified results of a rather interesting kind. In the former the stream-line from the apex just grazes the edge of the back plane and in

\* Communicated by the Author.

† Vol. xli. p. 801.

the latter it runs along its entire length, the stream dividing at the apex. When the angle of the wedge is small and the direction of the stream lies within it, the determining factor is found to be the ratio in which the wedge-angle is divided by the stream-direction. The actual magnitudes of the angles do not enter into the formulæ.

The following details are discussed :—

- (1) The ratio of the breadths in the two limiting cases. Incidentally it is shown that the free stream-line round the upstream edge of a single plane approaches a definite form of curve as the angle of attack is decreased, while, of course, the scale of the curve decreases to zero.
- (2) The ratio of the thrusts, in the Bobyleff case ; also, the loss of thrust brought about by the flow of the liquid along the rear plane when this extends so far as to bring the point of division of the stream to the corner.
- (3) The manner in which the velocity of the liquid varies along the planes from zero, where the stream divides, to the full value at the edge where the free stream-line begins.

### 1. *The Ratio of the Breadths.*

It will be convenient to begin with a summary of the analysis of the case where an infinite stream divides at the apex of a wedge and flows along its faces. Bobyleff solved this for an equal-sided wedge and symmetrical impact. When the direction of the stream makes unequal angles with the faces their breadths must have a definite ratio, the broader plane being that which is met at the smaller angle. By flattening out the wedge we can get the case of a single lamina.

Let the angle of the wedge be  $\gamma = \pi/n$ , and let  $\alpha$  and  $\beta$  be the parts into which it is divided by the direction of the stream. The configuration in the planes of

$$\begin{aligned} z &= x + iy, \\ w &= \phi + i\psi, \\ \Omega &= \log \left( -Q \frac{dz}{dw} \right), \\ &= \log_q Q + i\theta, \end{aligned}$$



and the corresponding values of the auxiliary real variable  $u$ , are shown on fig. 1. Then

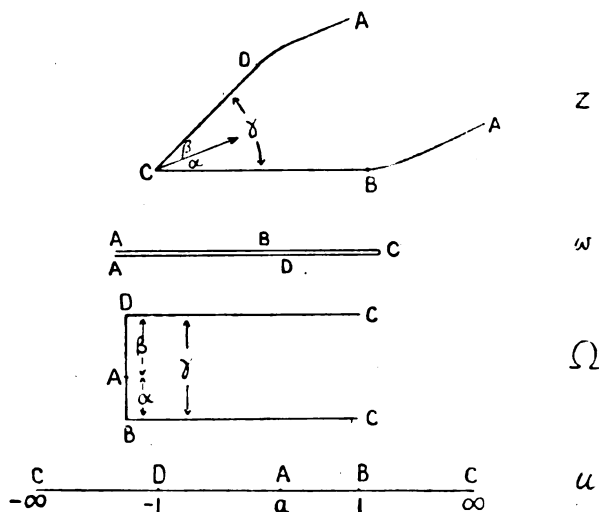
$$d\Omega/du = A(u^2 - 1)^{-1/2},$$

$$dw/du = B(u - a)^{-3}.$$

It is easily found that  $A = 1/n$ , and so

$$\Omega = \frac{1}{n} \log \{u + (u^2 - 1)^{1/2}\}.$$

Fig. 1.



Along the free stream-line,  $u = \cos n\theta$  and in particular, for the point at infinity,  $a = \cos n\alpha$ .

$$dz/du = -B\{u + (u^2 - 1)^{1/2}\}^{1/n} / Q(u - a)^3.$$

For points on the faces of the wedge, where  $|u| > 1$ , we obtain compact formulæ by introducing a new angular variable  $\chi$  connected with  $u$  by the equation

$$u = (1 + a \cos n\chi) / (a + \cos n\chi).$$

At the points C, B the values of  $\chi$  are  $\beta$  and zero. The length of the face CB is found to be equal to

$$\frac{2Bn}{Q \sin^4 n\alpha} \int_0^\beta \sin^{1+\frac{1}{n}} \frac{1}{2}n(\beta + \chi) \cdot \sin^{1-\frac{1}{n}} \frac{1}{2}n(\beta - \chi) \cdot \sin n\chi \cdot d\chi.$$

Now suppose  $n$  to become large. The angles  $n\alpha, n\beta$  remain finite, being  $\alpha\pi/\gamma, \beta\pi/\gamma$ . The expression for the length CB reduces to  $B/8Q \sin^4 \frac{1}{2}n\alpha$ . CD is got by putting  $\beta$  for  $\alpha$ . CB, CD may be called the  $\alpha$ -side and the  $\beta$ -side of the wedge. We have found that

$$\beta\text{-side}/\alpha\text{-side} = \sin^4 \frac{1}{2}n\alpha / \sin^4 \frac{1}{2}n\beta = \tan^4 \frac{\alpha}{\gamma} \frac{\pi}{2}.$$

This is the "Bobyeff ratio."

It is interesting to compare with the formula just obtained certain numerical results which have been worked out for me by Miss F. M. Chambers, M.Sc., using the exact formulæ and evaluating the integrals by planimeter. The values of  $\gamma$  can scarcely be regarded as "small," but the results are in satisfactory agreement.

$\gamma$ .	$\alpha$ .	Ratio by Planimeter.	By Formula.
15°	5°	9	9
18	5	20.6	21.64
20	5	30.7	33.97
22½	5	52	56.98

To find the other limiting ratio we must consider the free stream-line from the upstream edge of a single plane and find where it is met by a second plane, set off in the dead water at angle  $\gamma$  with the first.

Making  $n=1$  in the above analysis and putting  $u=\cos \theta$  we easily find for the coordinates of a point on the stream-line referred to the upstream edge ( $\theta=\pi$ )

$$x=c \int_{\pi}^{\theta} \sin \theta \cos \theta d\theta$$

$$y=c \int_{\pi}^{\theta} \frac{\sin^2 \theta d\theta}{(\cos \alpha - \cos \theta)^3}$$

where  $c$  is written for the length  $B/Q$ . ...

As  $\alpha \rightarrow 0$  the integrated values approach

$$x = \frac{1}{8}c \cot^2 \frac{1}{2}\theta (\cot^2 \frac{1}{2}\theta - 2),$$

$$y = \frac{1}{3}c \cot^3 \frac{1}{2}\theta.$$

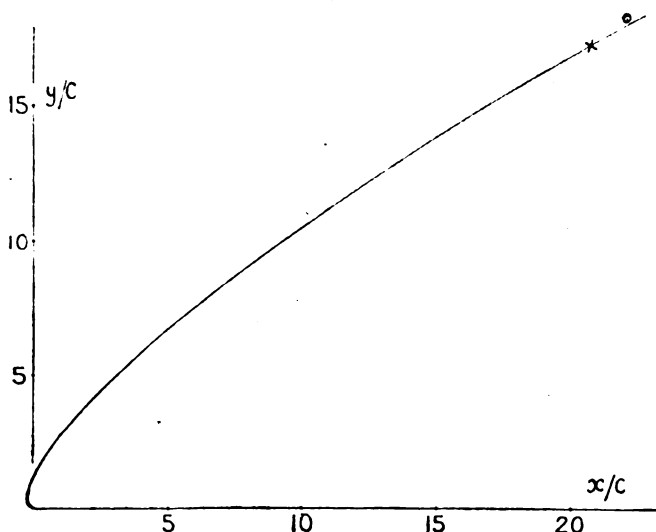
So that the equation to the limiting form for small angles of attack may be written

$$8x/c = \{1 - (3y/c)^{2/3}\}^2 - 1.$$

The curve turns to the right at  $\theta = \frac{1}{2}\pi$ ,  $x = -\frac{1}{8}c$ ,  $y = \frac{1}{3}c$ , and crosses the  $y$ -axis again at  $\theta = \cos^{-1} \frac{1}{3}$ ,  $y = 2\sqrt{2}c/3$ . Close to the edge it approximates to a semi-cubical parabola.

The curve is plotted on fig. 2. For comparison I have calculated some points on the exact curve for  $\alpha=5^\circ$ . Within the limits of the diagram the two curves are indistinguishable on this scale. The extreme points marked with a cross and a circle are the approximate and exact points for  $\theta=30^\circ$ .

Fig. 2.



At very distant points, as  $\theta=5^\circ$  is approached, the divergence, of course, becomes great, as is seen from the following table of coordinates.

	Exact Curve.		Approximate Curve.	
	$x$ .	$y$ .	$x$ .	$y$ .
150°.....	-.017	.006	-.017	.006
120 .....	-.070	.065	-.069	.064
90 .....	-.126	.336	-.126	.333
60 .....	.384	1.760	.375	1.732
30 .....	22.087	18.295	20.767	17.331
10 .....	3754.076	841.557	2100.9	497.76

Although this approximation gives a good idea of the form of the stream-line leaving the edge, it obviously cannot be used to obtain the intersection with a radius-vector making a small angle with the axis of  $x$ , for at the distant point where this meets the stream the angles  $\alpha$  and  $\theta$  are comparable in magnitude; we therefore go back to the exact

expressions for  $(xy)$  which, on integration, are found to be

$$\frac{x}{c} = \frac{2 + \cos \alpha}{2(1 + \cos \alpha)^2} + \frac{2 \cos \theta - \cos \alpha}{2(\cos \alpha - \cos \theta)^2},$$

$$\frac{y}{c} = \frac{1}{2 \sin^3 \alpha} \left\{ \frac{\sin \alpha \sin \theta (1 - \cos \alpha \cos \theta)}{(\cos \alpha - \cos \theta)^2} - \log \frac{\sin \frac{1}{2}(\theta + \alpha)}{\sin \frac{1}{2}(\theta - \alpha)} \right\}.$$

Making  $\theta, \alpha$  small and retaining only the terms of the largest order,

$$\frac{x}{c} = \frac{2}{(\theta^2 - \alpha^2)^2},$$

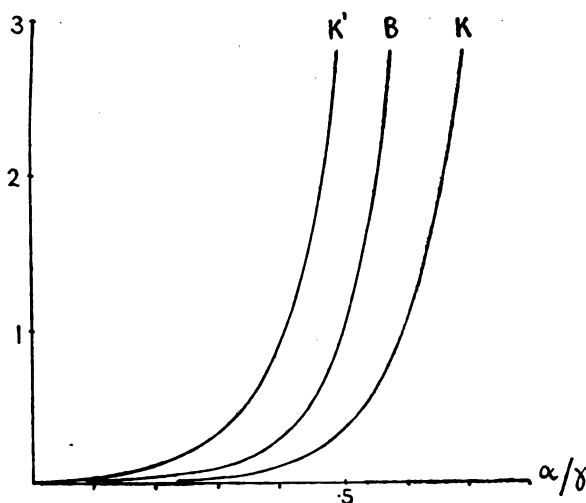
$$\frac{y}{c} = \frac{1}{2\alpha^3} \left\{ \frac{2\alpha\theta(\theta^2 + \alpha^2)}{(\theta^2 - \alpha^2)^2} - \log \frac{\theta + \alpha}{\theta - \alpha} \right\}.$$

At the point where the second plane reaches the stream-line  $y = \gamma x$ . So

$$\frac{\gamma}{\alpha} = \frac{\theta(\theta^2 + \alpha^2)}{2\alpha^3} - \frac{(\theta^2 - \alpha^2)^2}{4\alpha^4} \log \frac{\theta + \alpha}{\theta - \alpha}.$$

The breadth of the first plane is  $c(\pi \sin \alpha + 1)/2 \sin^4 \alpha$ , which may be put  $= 2c/\alpha^4$ . The required approximate ratio is then  $x/\text{breadth of plane} = \alpha^4/(\theta^2 - \alpha^2)^2$ . Thus assuming a value

Fig. 3.



for  $\theta/\alpha$  (being  $>1$ ) we can find the corresponding associated values of  $\alpha/\gamma$  and of the breadth ratio, which can then be plotted together.

On fig. 3 the curves marked B and K show the Bobyleff

and Kirchhoff ratios for different values of  $\alpha/\gamma$ . They may be compared with the corresponding and similar curves given in the previous paper for a right-angled wedge. The curve marked K' shows, over any value of  $\alpha/\gamma$ , the reciprocal of the K-ratio for  $1 - \alpha/\gamma$  or  $\beta/\gamma$ .

As an illustration of the information contained in this diagram suppose a wedge-shaped blade to be met by a stream at an angle of  $5^\circ$ . Take the breadth of the front face of the blade as unity and suppose a back face making an angle of  $15^\circ$  with the front one, to be extended to an increasing breadth. Then, over the value  $\alpha/\gamma = \frac{1}{3}$ , three critical breadths are indicated, separating four distinct types of motion :

(1) While the back face lies altogether in the dead-water region, the stream divides very near the edge on the front face. Calculation for  $\alpha = 5^\circ$  shows that the distance from the edge to the point of division is less than  $1/50,000$  of the breadth of the plane. When the back plane reaches a breadth of about  $\cdot 05$  (on the curve K), it interferes with the stream-line.

(2) After this a small pocket of dead water is formed at the edge, on the back plane, beyond which the stream-line runs along the remaining distance of this plane to its further edge. The point of stream-division comes still nearer to the edge on the front plane. There is, of course, a loss of thrust. When the breadth of the back plane reaches about  $\cdot 11$  we are on the B-curve. The stream divides at the angle of the wedge. In the next part of the work we shall find an approximate value for the loss of thrust at this stage.

(3) The point of division of the stream now comes on the back face, and a pocket of dead water is formed on the front face at the edge. With further extension of the rear plane this pocket spreads until, on the curve K', for breadth of about  $\cdot 45$ , it covers the whole of the front face. At some point in this stage the resultant thrust vanishes and then reverses.

(4) With further extension we get the original motion with the rôles of the planes reversed and an incidence on the other face at an angle  $10^\circ$ .

By following a horizontal instead of a vertical line across the diagram the effect of changing the angle of incidence can be followed in a similar manner.

Without claiming for this investigation any direct application to practical conditions, one may, perhaps, infer from it that with small angles of attack the nature of the motion and the magnitude of the thrust obtained will be sensitive to comparatively small changes in the geometrical configuration.

As a test of the closeness of the Kirchhoff approximation I have calculated the coordinates of the point  $\theta=10^\circ$  on the accurate stream-line for  $\alpha=5^\circ$ . I find that the radius vector makes an angle of  $12^\circ 38'$  with the plane and that its length is  $\cdot 104$  of the breadth of the plane. The value of  $\alpha/\gamma$  is  $\cdot 396$  and the height of the K-curve for this abscissa is about  $\cdot 11$ .

## 2. Thrusts on the Planes.

At a point on the plane CB we have the velocity

$$q = Q\{u + (u^2 - 1)^{\frac{1}{2}}\}^{-\frac{1}{n}},$$

or, in terms of the angle  $\chi$  already used,

$$q = Q \sin^{-\frac{1}{n}} \frac{1}{2}n(\beta + \chi) \cdot \sin^{\frac{1}{n}} \frac{1}{2}n(\beta - \chi).$$

The excess pressure

$$\begin{aligned} p &= \frac{1}{2}\rho(Q^2 - q^2) \\ &= \frac{1}{2}Q^2\rho \left\{ 1 - \sin^{-\frac{2}{n}} \frac{1}{2}n(\beta + \chi) \cdot \sin^{\frac{2}{n}} \frac{1}{2}n(\beta - \chi) \right\}. \end{aligned}$$

Multiplying by the element of length and integrating along the plane, we obtain for the thrust on CB

$$\begin{aligned} \frac{BQ\rho n}{\sin^4 n\alpha} \int_0^\beta \left\{ \sin^{1+\frac{1}{n}} \frac{1}{2}n(\beta + \chi) \cdot \sin^{1-\frac{1}{n}} \frac{1}{2}n(\beta - \chi) \right. \\ \left. - \sin^{1-\frac{1}{n}} \frac{1}{2}n(\beta + \chi) \sin^{1+\frac{1}{n}} \frac{1}{2}n(\beta - \chi) \right\} \sin n\chi d\chi. \end{aligned}$$

When  $n$  becomes large the expression for  $p$  approaches the value

$$\frac{1}{2}Q^2\rho \cdot \frac{2}{n} \log \frac{\sin \frac{1}{2}n(\beta + \chi)}{\sin \frac{1}{2}n(\beta - \chi)},$$

and the approximate value of the thrust is

$$\begin{aligned} \frac{2BQ\rho}{\sin^4 n\alpha} \int_0^\beta \sin \frac{1}{2}n(\beta + \chi) \cdot \sin \frac{1}{2}n(\beta - \chi) \cdot \sin n\chi \\ \times \log \frac{\sin \frac{1}{2}n(\beta + \chi)}{\sin \frac{1}{2}n(\beta - \chi)} \cdot d\chi. \end{aligned}$$

This can be integrated by parts; the result is

$$\begin{aligned} \left[ \frac{1}{4} \sin n\beta (\sin n\chi - n\chi \cos n\beta) \right. \\ \left. - \frac{1}{4} (\cos n\chi - \cos n\beta)^2 \log \frac{\sin \frac{1}{2}n(\beta + \chi)}{\sin \frac{1}{2}n(\beta - \chi)} \right]_0^\beta, \end{aligned}$$

omitting the factor  $2BQ\rho/n \sin^4 n\alpha$ .

The logarithmic term vanishes at both limits, and we obtain for the thrust

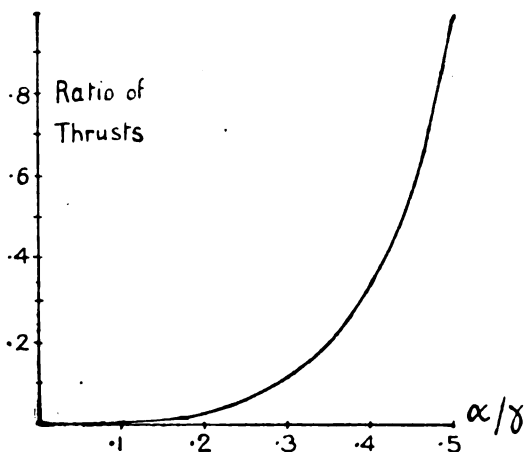
$$BQ\rho(\sin n\beta - n\beta \cdot \cos n\beta)/2n \sin^3 n\alpha.$$

It follows that thrust on  $\alpha$ -side : thrust on  $\beta$ -side

$$= \left(1 - \frac{\beta}{\gamma} \pi \cot \frac{\beta}{\gamma} \pi\right) : \left(1 - \frac{\alpha}{\gamma} \pi \cot \frac{\alpha}{\gamma} \pi\right).$$

The graph of this ratio is shown on fig. 4. I add a table

Fig. 4.



giving the values found by planimeter for the four cases referred to in the preceding paragraph, along with those given by the approximate formula. In the first of these the areas were too small to give an accurate measurement.

$\gamma$ .	$\alpha$ .	Ratio by Planimeter.	By Formula.
15°	5°	6.8	5.58
18	5	12.9	12.67
20	5	13.2	13.64
22½	5	27.9	22.3

If now the two faces are taken together, the resultant thrust on the wedge, when the angle is small, may be taken as the

difference of the thrusts on the two faces. Its magnitude is

$$BQ\rho\gamma \cos n\alpha/2 \sin^3 n\alpha.$$

Dividing by the breadth of the front face, which is  $B/8Q \sin^4 n\alpha$ , we get for the thrust per unit breadth the expression

$$Q^2\rho\gamma \sin \frac{1}{2}n\alpha \cdot \cos n\alpha/2 \cos^3 \frac{1}{2}n\alpha.$$

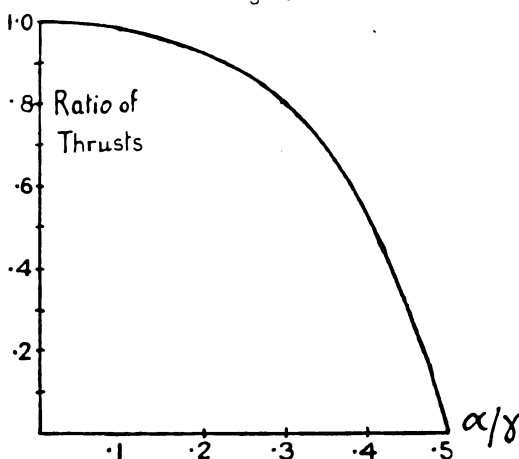
If the back plane were absent the thrust per unit breadth would be  $\frac{1}{4}Q^2\rho\pi\alpha$  and so the effect of the back plane, at this particular breadth, is to reduce the thrust by the factor

$$\sin \frac{1}{2}n\alpha \cdot \cos n\alpha/\frac{1}{2}n\alpha \cdot \cos^3 \frac{1}{2}n\alpha$$

$$(n\alpha = \frac{\alpha}{\gamma} \cdot \pi).$$

This function is plotted against  $\alpha/\gamma$  on fig. 5.

Fig. 5.



Returning to fig. 3 we see that the above work has given the decrease in the effective thrust brought about as the breadth of the second plane increases from  $k$ , when it first interferes with the motion of the liquid, to  $b$  when the streamline divides at the apex,  $k b k'$  being used for the ordinates of the three curves. The negative thrust for breadth  $k'$  is also known; its ratio to the original thrust on the single plane is evidently  $k'\beta/\alpha$ . With these data it is further possible to get a rough estimate of the breadth of the second plane



which makes the resultant thrust vanish, if we make the assumption that the decrease of thrust is connected by an approximately linear relation with the increase of breadth of the second plane. This procedure would be suggested if the proportionality between decrease of thrust and increase of breadth were found to hold between the critical cases which have been discussed. This is exactly the case when the direction of the stream bisects the angle of the wedge, for then we have

$$\begin{array}{llll} \text{thrust 1 for breadth } k, & & & \\ \text{,, } 0 & \text{,, } 1, & & \\ \text{,, } -k' & \text{,, } k'. & & \end{array}$$

Readings taken from figs. 3 and 5 show that the relation holds approximately for other values of  $\alpha/\gamma$  which are not too small to permit of accurate readings. It is otherwise evident that a graph for this fourth critical value of the breadth, lying between B and K', is roughly determined by the conditions of touching the axis at the origin and passing through the point (0.5, 1).

### 3. *Variation of Velocity along the Planes.*

Comparatively simple relations between the velocity of the liquid and the distance, measured from the point of zero velocity, can be found in certain cases, and from these the distribution of thrust over the planes.

Using the angle  $\chi$  as before and considering the plane CB in the general Bobyleff case, we have for the distance of a point from the apex

$$x = A \int_{\chi}^{\beta} \sin^{1+\frac{1}{n}} \frac{1}{2}n(\beta + \chi) \cdot \sin^{1-\frac{1}{n}} \frac{1}{2}n(\beta - \chi) \cdot \sin n\chi \cdot d\chi,$$

with

$$\eta = \sin \frac{1}{2}n(\beta + \chi) / \sin \frac{1}{2}n(\beta - \chi).$$

The constant A will be given such a value as will make  $x=1$  along with  $\eta=1$  at the edge where  $\chi=0$  and the free streamline begins.

The integral for  $x$  can be evaluated in two cases,

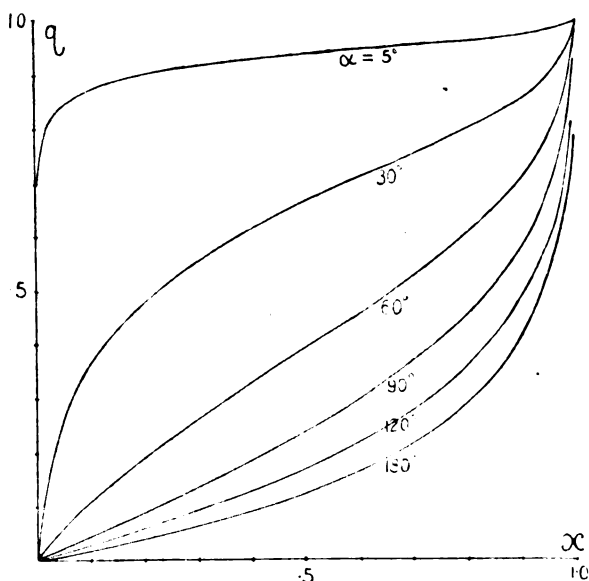
- (a) when the wedge flattens out to a plane,
- (b) when, as in the previous work,  $n$  is large.

(a). Replacing  $\beta$  by  $(\pi - \alpha)$  the expression for  $x$  becomes

$$A \{ 2(\cos \chi + \cos \alpha) + \sin(\chi + \alpha) \cdot \sin(2\alpha - \chi) - (\pi - \alpha - \chi) \sin \alpha \}.$$

The result of plotting  $q$  against  $x$  for different angles of incidence is shown on fig. 6.

Fig. 6.



A curious feature of these curves is seen in the approach to a limiting form as the angle  $\alpha$  approaches  $\pi$ , i. e. on the short upstream side in the case of very oblique incidence. The equation to this limiting graph is found by replacing  $\chi$  by  $(\pi - \chi)$  in the above, and expanding in powers of the small angles  $\chi\alpha$ . The lowest order which does not vanish is the fourth. The result is

$$x = (\alpha - \chi)(17\alpha^3 + 17\alpha^2\chi + 11\alpha\chi^2 + 3\chi^3)/17\alpha^4,$$

making  $x=1$  when  $\chi=0$ . Along with this

$$q = (\alpha - \chi)/(\alpha + \chi).$$

Elimination of  $\chi/\alpha$  gives the algebraic equation

$$x = 16q(q^3 + 4q^2 + 6q + 6)/17(1 + q)^4.$$

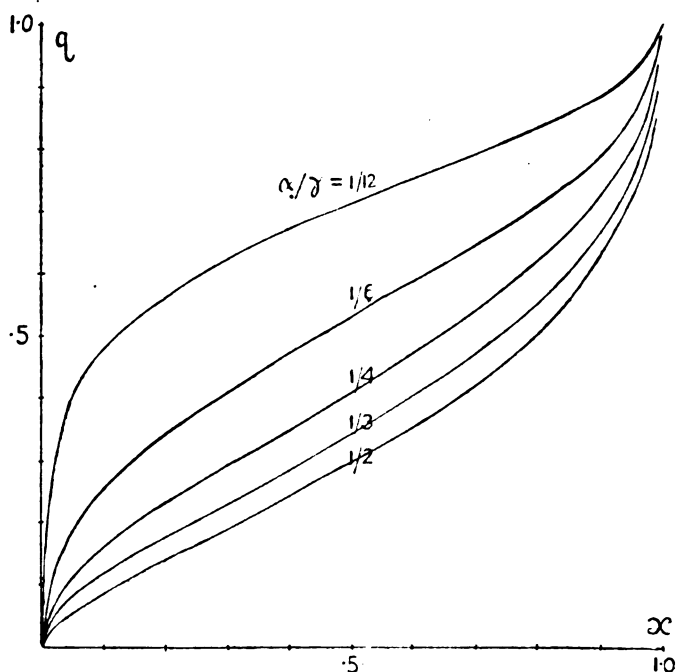
(b). By means of the approximations already used we obtain

$$x = (\cos n\chi - \cos n\beta)^2 / (1 - \cos n\beta)^2.$$

It is now easy to eliminate  $\chi$  and connect  $xq$  directly. The result is

$$x = \left\{ 4q \sin^2 \frac{\alpha \pi}{\gamma^2} / (1 - 2q \cos \frac{\alpha}{\gamma} \pi + q^2) \right\}^2.$$

Fig. 7.



The graphs are shown on fig. 7. They agree closely with results obtained by planimeter in the special cases already referred to.

L. *The Crystal Structures of the Rhombohedral Forms of Selenium and Tellurium.* By A. J. BRADLEY, M.Sc., Research Student in Physics, The Physical Laboratories, University of Manchester\*.

[Plate X.]

A. SELENIUM.

1. *Introductory.*

ACCORDING to Groth†, selenium crystallizes in three modifications, of which two belong to the monoclinic system, and the third to the rhombohedral system. The last form, known as metallic selenium, is isomorphous with the naturally occurring crystals of tellurium. It has a specific gravity of about 4·8‡, and crystallizes in small hexagonal prisms. There is no record of crystals being obtained sufficiently good to give any definite value for the interfacial angles and the axial ratio. F. C. Brown§ describes the production of crystals of metallic selenium of three distinct types by distillation at various temperatures and under varying partial pressures of selenium vapour. The first type were rhombohedral or hexagonal in shape, and agreed with Muthmann's description. Other crystals grew in clusters of spines or needles. These acicular crystals were quite stiff and tough, in striking contrast with the third type, which consisted of flexible sheets, the thickness being of the order of 0·01 mm. These lamellar crystals were produced when the temperature was low.

2. *Experimental.*

The crystal structure was investigated by the method of the powder photograph. The experimental arrangements were exactly the same as in the case of arsenic||. The first photographs obtained were from the finely-divided grey selenium, the particles of which were too small to show any lustre. Not many lines were visible, and these were weak, broad, and indistinct. There was very much general blackening of the film, which indicates the presence of a large proportion of amorphous material. Only approximate

\* Communicated by Prof. W. L. Bragg, F.R.S.

† *Chemische Krystallographie*, i. p. 33 (1906).

‡ Muthmann, *Zeitschr. f. Krystall.* xvii. p. 354 (1890).

§ *Phys. Rev.* (2) iv. p. 85 (1914).

|| A. J. Bradley *Phil. Mag.* xlvii. p. 657 (1924)

measurements could be made, but these were sufficient to indicate the nature of the space-lattice. By comparing the observed spacings with those given by Hull's \* graph for a simple triangular lattice, an agreement was found for an axial ratio of about 1.14. Density considerations show that each point of the lattice represents three atoms of selenium. No further progress could be made in the elucidation of these films, so an attempt was made to grow some larger crystals of selenium, and in this way to obtain a mass of material free from amorphous diluents.

The crude vitreous selenium was placed in a glass cylindrical vessel which was carefully evacuated, and the selenium was heated by placing the cylinder vertically with the lower end in an electrically-heated jacket. After several days crystals appeared in the cooler portion of the vessel. The sublimate formed three well-marked zones. First, nearest the heated end, was a sharply-defined narrow horizontal zone of definitely crystalline material, which ultimately grew almost across the tube. Then followed a broad band of shiny grey scales covering the walls of the vessel, which gradually gave way to a still broader zone consisting of an attenuated red film.

The crystals were of the lamellar type, about a centimetre long and about 0.4 mm. across. In general appearance they resembled the crystals described by Brown (*loc. cit.*). No other form of crystal was observed.

A sample of these lamellar crystals was ground in an agate mortar and exposed to X-rays in the usual manner. The photograph so obtained was identical with the earlier films in respect to the positions of the lines, but the intensities were not all in the same relative order in the two sets of films. The most obvious explanation of this difference is to be found in the large size of the crystalline particles in the second experiment. In order to test this hypothesis, two more exposures were made with more carefully-ground specimens of the recrystallized selenium. A comparison of the intensities showed that in both cases the lines were in almost the same order of intensity as those on the film taken with the crude material, though one or two lines showed a tendency to deviate towards the order given by the coarsely-ground specimen. The orders of intensity are given in Table I. They were obtained by the method already described in the case of arsenic (*loc. cit.*). Column IV. refers to a film taken with the crude material; Column V.

\* A. W. Hull, Phys. Rev. (2) xvii. p. 571 (1921).

was obtained from the coarse crystals; and Columns VI. and VII. from the more finely-ground specimen.

TABLE I.

I.	II.	III.	V. Order of Intensity.			VII.
			IV.	Large crystals.	Small crystals.	
$\frac{d}{n}$ (Obs.) $\times 10^{-3}$ cm.	$\frac{d}{n}$ (Calc.) $\times 10^{-3}$ cm.	Reflecting Planes.	Powder.			
...	4.96	0001	...	...	...	...
3.71	3.77	1010	3	2	3	4
2.982	2.999	1011	1	1	1	1
...	2.480	0002	...	...	...	...
2.174	2.175	1120	...	6	6	9
2.070	2.071	1012	2	3	2	2
1.998	1.990	1121				
1.891	1.883	2020	...	16	18	18
1.761	1.762	2021	4	4	4	3
1.639	1.653	0003	5	10	7	5
	1.634	1122				
1.502	1.511	1013	6	10	7	5
	1.499	2022				
1.430	1.423	1230	8	5	5	5
1.371	1.370	1231	...	12	12	14
1.315	1.315	1123	...	15	13	12
1.271	1.256	3030	...	19	19	19
1.241	1.241	2023	..	9	10	10
	1.240	0004				
	1.234	1232				
1.220	1.217	3031				
1.177	1.176	1014	...	15	15	15
1.122	1.119	3032	...	14	13	13
1.079	1.087	2240	7	7	9	8
	1.077	1233				
	1.075	1124				
1.061	1.063	2241				
1.043	1.045	1340	..	20	20	20
1.025	1.034	2024	...	8	11	11
	1.022	1341				
.997	.999	2242	...	17	17	17
	.995	3053				
.963	.963	1342	...	17	16	16
	.957	1015				

It appears from a comparison of the photographs obtained with the coarse and finely-divided material, that in the former case there is a tendency for planes which make small angles with the trigonal axis to give too great a relative intensity of reflexion. Thus in Column V., lines belonging to planes (1010), (2020), (1120) are all too strong, whereas

those corresponding to planes (0003), (1122), (1013), (2022) are all too weak. This is probably due to the lamellar nature of the crystals, which favours a definite orientation.

### 3. Selection of a possible Structure for Selenium.

The film whose order of intensity is given in Column VII. was the clearest obtained, and hence measurements from this film were used to find the lattice dimensions. The calculations were similar to those for arsenic (*loc. cit.*), and Column I. gives the values of  $\frac{d}{n}$  obtained in this way.

Every line which appeared on the first photographs with the crude material is repeated on this film, but in addition many lines which were there too faint to show up, now appear. Only those spacings are present which fit on Hull's graph for a triangular lattice of axial ratio  $c:a=1.14:1$ . Two important lines, however, are still missing. This omission affords a valuable clue to the structure, as will be seen later.

From Hull's graph we can also obtain the indices of the planes corresponding to each line on the film. Thus the spacing  $\frac{d}{n}=1.89 \text{ \AA.}$  corresponds to the plane (2020). The spacing of (10 $\bar{1}$ 0) planes is therefore  $3.78 \text{ \AA.}$  This value is chosen in preference to that obtained from the first-order reflexion on account of the much greater sharpness of the lines (2020). The volume of the unit cell, which is a right rhombic prism and contains one point of the lattice, is  $\frac{4}{3}d_{10\bar{1}0}^3 \times 1.14 = 82.0 \times 10^{-24} \text{ c.c.}$ , where  $d_{10\bar{1}0}$  is the spacing of planes (1010). Assuming the density of selenium to be 4.8 and its atomic weight 79.2, and taking the weight of the hydrogen atom as  $1.663 \times 10^{-24} \text{ gm.}$  and its atomic weight as 1.008, the volume occupied by one atom of selenium is  $27.24 \times 10^{-24} \text{ c.c.}$  The number of atoms associated with each point of the lattice is therefore  $\frac{82.4}{27.24} = 3.01$ . In other words, the structure consists of three interpenetrating lattices.

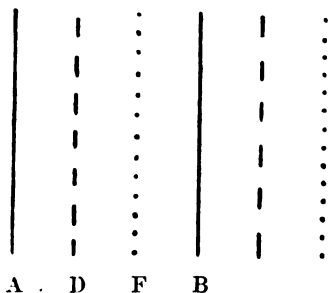
Every value of  $\frac{d}{n}$  within a certain range was then calculated for such a system and for the constants given above. These values agreed with the observed values of Column I., but were on the whole 0.1 per cent. too high. After correcting for this difference, the calculated values are

given in Column II. From these corrected values we obtain the length of the side of the base of a unit cell,  $a=4.35 \text{ \AA}$ . This confirms the results obtained by Miss M. K. Slattery\*, who found that the structure of selenium consisted of a simple triangular lattice of axial ratio 1.14 and length of side of base  $4.34 \text{ \AA}$ , three atoms being associated with each point of the lattice. The corrected density will be 4.82.

It is interesting to compare these results with the observations of F. C. Brown† on the lamellar crystals of selenium. Brown considered that these crystals belonged to the monoclinic system, axial ratio  $a:b:c=1.0:0.18:6.0$ ;  $\beta=60^\circ$ . As the ratio  $c:a$  is an integer and the angle  $\beta$  is  $60^\circ$ , it seems likely that the crystals are really trigonal. All the X-ray data fit in with this assumption, and measurements of lamellar crystals which I have made point to the same conclusion. The crystals appear to be composite, consisting of a number of parallel growths. In one case a single crystal of measurable dimensions was isolated from a lamellar crystal, which possessed clearly-defined trigonal symmetry. It gave values for the interfacial angles  $(1011):(1101)$ ,  $\alpha=87^\circ 36'$ , corresponding to an axial ratio  $c:a=1.15$ . It does not seem likely that there is any difference in structure between Brown's three forms of selenium, especially in view of his own observations on the identity of the electrical, light electric, and electro-mechanical properties of selenium crystals of the three forms.

It remains to discover the mutual orientation of the three lattices which compose the selenium structure. All the

Fig. 1.



spacings tabulated in Column II. have their counterpart in Column I. except (0001) and (0002). The spacing (0001) of a single lattice (AB in fig. 1) must therefore be divided

\* Phys. Rev. (2) xxi. p. 378 (1923).

† Phys. Rev. (2) v. p. 236 (1915).



by the planes D and F belonging to the other lattices, so that  $AD=DF=FB$ ; the first reflexion will correspond to AD, the (0003) spacing.

Further elucidation of the structure depends upon considerations of symmetry. Assuming the crystals to be trigonal, their structure must constitute a Sohncke \* point system †. There are only eight such systems possessing trigonal symmetry, in which the spacing (0001) is divided by three. Hexagonal point systems can be ruled out, as they require at least six atoms to each point of the triangular lattice. Five of these trigonal systems possess 2—al axes of symmetry, namely:—

1. Nos. 19 and 20.—Right and Left compound 3-point screw systems.
2. No. 22.—Compound Rhombohedron system.
3. Nos. 23 and 24.—Right and Left alternating 3-point screw systems.

Systems 19 and 23 are the mirror images of systems 20 and 24 respectively, the screws being in one case right-handed and in the other left-handed.

In point systems Nos. 19, 20, 23, and 24 there are in general six points grouped in pairs round each point of the simple triangular lattice; the pairs are symmetrical about the three 2—al axes. In the present case we have only three atoms to each lattice point, so that in place of three pairs of points, there is a single point on each of the three 2—al axes. System 22 has in general eighteen atoms to each lattice point. If we simplify this by reducing the number of atoms to three, the structure becomes a simple rhombohedral lattice. Such an arrangement is impossible for selenium, as reflexions from many of the wider spacings which actually occur could not then be given.

The conditions for systems 19, 20, 23, 24 are completely satisfied by the observed spacings.

Fig. 2 gives a projection of systems 19 and 20, and fig. 3 of systems 23 and 24, the trigonal axes being perpendicular to the plane of the paper. Differently shaded circles represent atoms at different levels along the trigonal axes.

\* Sohncke, *Entwicklung einer Theorie der Kristallstruktur*, 1871.

† If not, the structure would possess operations of the second sort, and the atoms would occur in pairs, which is not the case.

Fig. 2.

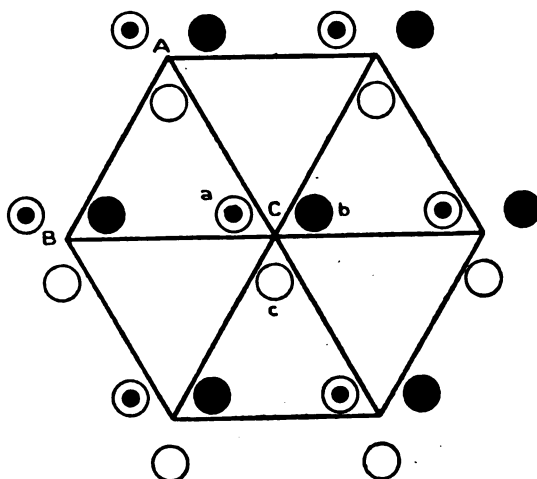
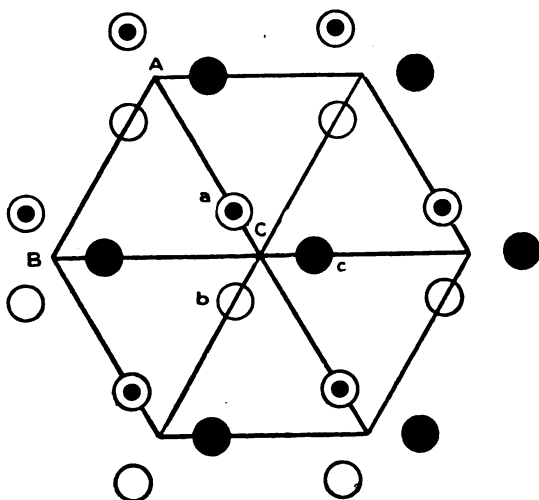


Fig. 3.



Each of these systems has an infinite number of parallel 3-*al* screw axes, and also an infinite number of non-intersecting 2-*al* axes, lying in planes perpendicular to the

3-*al* axes. Figs. 4 and 5 show the positions of the axes in systems 19 and 20, and 23 and 24 respectively. The 2-*al*

Fig. 4.

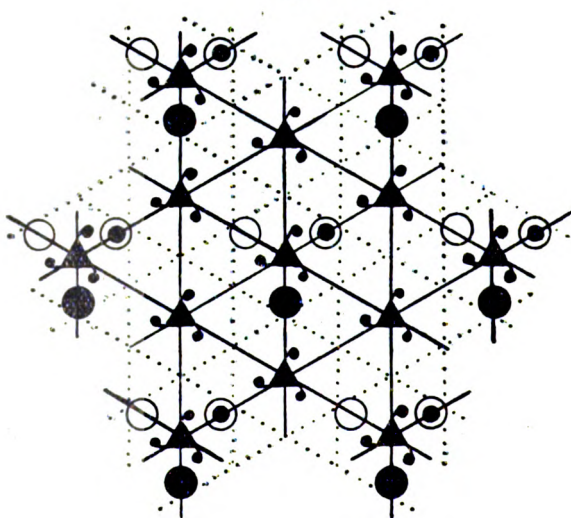
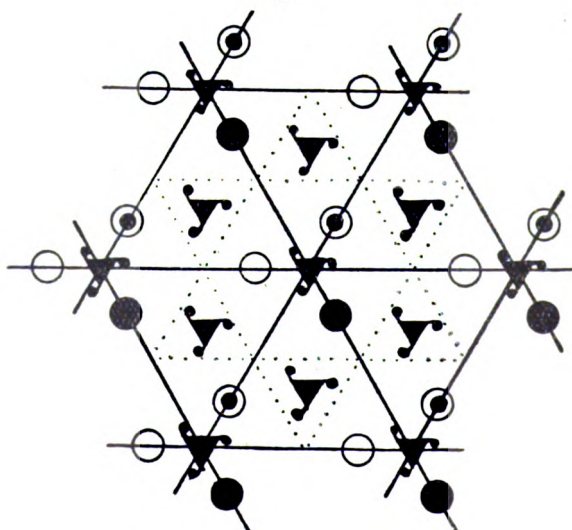


Fig. 5.



axes are of two kinds—rotatory (indicated by continuous lines) and screw (indicated by dotted lines). The arrangement of the axes in fig. 4 shows that the structure belongs to

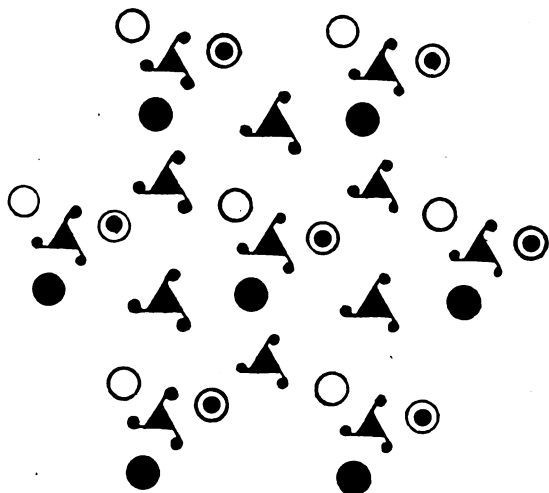
to the general space group \*  $D_3^3$  or  $D_3^5$ , and that shown in fig. 5 to the space group  $D_3^4$  or  $D_3^6$ . Both are isomorphous with the point group  $D_3$ , so that if selenium possesses either of these two types of structure, its symmetry will be trigonal holoaxial.

In each case there is a variable parameter—the ratio of the size of the small triangle  $abc$  to that of the large triangle  $ABC$  (figs. 2 and 3). Upon the value of this parameter depends the intensity of reflexion from all planes except (0001) for all orders of reflexion. It is therefore possible to test the validity of either of these structures by attempting to find a value for the variable parameter, which will give the observed intensities of reflexion. If such a value does not exist, the structure must be of another type.

Of the systems which are without 2-*al* axes, No. 18 can be ruled out immediately for similar reasons to those used for No. 22. There remain:—

Nos. 15 and 16.—Right and left three-point screw systems.

Fig 6.



These systems differ only from the four just considered in that the sides of the small triangle  $abc$  are now neither parallel nor perpendicular to the sides of the large triangle  $ABC$ . Fig. 6 shows a projection perpendicular to the trigonal axes of a possible structure belonging to this system. It is a space group  $C_3^2$  or  $C_3^3$ , and possesses only 3-*al* screw axes and no other elements of symmetry. It is isomorphous with the point group  $C_3$ , so that the crystal

\* Hilton, 'Mathematical Crystallography,' p. 222 (1903).

symmetry would be trigonal polar. As far as evidence from the crystal form can show, there is no reason for assigning the crystals to a class with such low symmetry; the other types of structure therefore seem preferable.

It can readily be shown that a structure based on systems 19 and 20 will not fit in with the experimental results. The observed orders of intensity of reflexion are given in Table II., Column III., and are the mean of the values<sup>§</sup> in

TABLE II.

I.	II.	III.	IV.	V.	VI.	VII.
Re- flecting Planes.	N $\sin \theta$	Observed Order of Intensity.	Calculated Order of Intensity. B=0.    B=3.4.		Calculated Equation (3).	Intensity Equation (4).
0001	...	...	...	...	...	...
1010	140.0	3	8	3	24.2	23.9
1011	180.1	1	1	1	51.0	49.5
0002	...	...	...	...	...	...
1120	47.8	9	12	9	8.21	8.00
1012	86.6	2	2	2	{ 19.1	18.4
1121	80.9				{ 15.3	14.8
2020	36.2	18	18	17	1.48	1.42
2021	62.8	4	7	4	13.5	13.0
0003	90.5	5	9	5	{ 2.80	3.65
1122	54.3				{ 8.0	7.70
1013	45.8	6	4	6	{ 3.74	3.55
2022	45.8				{ 7.75	7.38
1230	41.5	6	5	7	10.05	9.40
1231	76.2	13	16	12	3.27	3.09
1123	36.2	12	14	13	2.90	2.82
3030	16.4	19	20	20	.02	.02
0004	...	...	...	...	...	...
2023	31.3	10	10	10	{ .61	.58
1232	62.6				{ 2.15	2.01
3031	30.1				{ 3.50	3.27
1014	28.0	15	15	16	2.30	2.15
3032	25.6	13	13	15	2.33	2.18
2340	11.8	8	3	8	{ .79	.75
1233	47.2				{ 5.80	5.18
1124	23.6				{ 1.33	1.26
2241	22.8				{ 1.00	.94
1340	22.1	20	19	19	.31	.30
2024	21.3	11	6	11	{ 1.28	1.25
1341	42.6				{ 2.49	2.43
2242	20.1	17	17	18	{ .66	.68
3033	20.1				{ .01	.01
1342	39.5	16	11	14	{ 1.99	2.08
1015	19.76				{ .86	.90
Total error .....			41	10		

Table I., Columns IV., VI., and VII. If  $x$  is the ratio of  $ab$  to  $AB$  (fig. 2) it can be shown that for planes  $(h0h0)$  the phase factor is given by  $F = 5 + 4 \cos 2\pi xh$ . As the glancing angle increases, the observed reflexions for different orders fall away more quickly than they would normally do, judging from other lines on the film; hence

$$F_{10\bar{1}0} > F_{2020} > F_{3030} \cdot 2\pi x < 80^\circ.$$

For planes  $(h0hl)$  where  $l$  is not a multiple of 3,  $F = 2 - 2 \cos 2\pi xh$ . After allowing for the difference in the number of co-operating planes, a comparison of neighbouring lines on the film shows:—

1.  $(10\bar{1}1)$  is greater than  $(10\bar{1}0)$ ;  $2\pi x > 120^\circ$ .
2.  $(2021)$  is much greater than  $(2020)$ ;  $2\pi x$  lies between  $60^\circ$  and  $120^\circ$ .
3.  $(1014)$  and  $(3032)$  are almost equal;  $2\pi x = 90^\circ$  or  $180^\circ$ .  $2\pi x \nless 80^\circ$ .
4.  $(3030) < (10\bar{1}4)$  or  $(3032)$ ;  $2\pi x$  lies between  $45^\circ$  and  $80^\circ$ , or between  $160^\circ$  and  $180^\circ$ .

Only values of  $2\pi x$  between 0 and  $180^\circ$  have been considered, as all possible values of  $F$  occur within those limits. It is clear that no value of  $x$  can satisfy these conditions even approximately, so systems 19 and 20 can be definitely rejected. Only systems 23 and 24 remain.

#### 4. Confirmation of the Structure and Evaluation of the Indeterminate Parameter.

In systems 23 and 24 the atoms are arranged as follows:—

$$\begin{array}{lll} m, n, p; & m + 2x, n + x, p + \frac{1}{3}; & m + x, n - x, p + \frac{2}{3} \\ m + 1, n, p; & m + 2x + 1, n + x, p + \frac{1}{3}; & m + x + 1, n - x, p + \frac{2}{3} \\ m, n + 1, p; & m + 2x, n + x + 1, p + \frac{1}{3}; & m + x, n - x + 1, p + \frac{2}{3} \end{array}$$

where  $m, n, p$  are integers and  $x$  is the ratio of the distance  $aC$  to  $AC$  (fig. 3). The axes of reference are two axis at  $120^\circ$  to each other and at  $90^\circ$  to the third axis. The phase factor for planes  $(hkl)$  \* will therefore be given by:—

$$F_{hkl} = 3 + 2 \left\{ \cos \left( 2xh + xk + \frac{1}{3}l \right) 2\pi + \cos \left( xh - xk + \frac{2}{3}l \right) 2\pi + \cos \left( xh + 2xk - \frac{1}{3}l \right) 2\pi \right\} \quad (1)$$

The phase factors for all planes giving observed reflexions

\* I. e.  $(hki)$ . The index  $i$  being dependent on  $h$  and  $k$  is redundant for any calculations.

were tabulated for various values of  $x$  and plotted graphically for reference. Planes ( $h0\bar{h}l$ ), where  $l$  is not a multiple of 3, give two different values for the phase factor, depending on the signs of  $h$  and  $l$ . There are an equal number of planes giving each value, so that  $F_{h0l}$  has been defined as the mean value given by equation (1). With this definition, values of  $F_{hkl}$  for  $2\pi x$  between 0 and  $\pi$  are the same as for  $2\pi x$  between  $2\pi$  and  $\pi$ , so that only values of  $2\pi x$  below  $180^\circ$  need be considered.

At this stage it is convenient to take into account the gradual falling-off in intensity with increase of glancing angle. This is due to many independent factors, such as the effect of electron distribution within the atom. The resultant effect may be expressed in the form

$$I \propto f'(\theta),$$

where  $I$  is the total intensity of reflexion at a glancing angle  $\theta$ , and  $f'(\theta)$  is an unknown function of  $\theta$ . The intensity of reflexion is also proportional to the number of faces  $N$  corresponding to the form  $\{hkl\}$ . Combining these factors with the phase factor, the intensity of reflexion from a plane ( $hkl$ ) is given in arbitrary units by

$$I = NF_{hkl}f'(\theta). \quad (2)$$

As a first approximation only, we assume that  $f'(\theta) = \text{cosec}^2 \theta$ , as in the case of arsenic (*loc. cit.*). In order to minimise any error introduced by this assumption, only lines in neighbouring portions of the film are compared.

Table II., Column II. gives the values of  $\frac{N}{\sin^2 \theta}$  for various reflecting planes, and comparing this with Column III. for neighbouring lines, we see that the following conditions must hold :—

1. ( $10\bar{1}1$ ) is much stronger than ( $10\bar{1}0$ ) ;  $2\pi x > 64^\circ$ .
2. ( $1120$ ) is far less than half ( $1011$ ) ;  
 $2\pi x$  lies between  $42^\circ$  and  $108^\circ$  or above  $132^\circ$ .
3. ( $1120$ ) is far greater than twice ( $2020$ ) ;  
 $2\pi x$  lies between  $39^\circ$  and  $148^\circ$ .
4. ( $2020$ ) is much less than a quarter ( $2021$ ) ;  
 $2\pi x$  lies between  $40^\circ$  and  $140^\circ$ .
5. ( $12\bar{3}1$ ) is far less than ( $12\bar{3}0$ ) ;  
 $2\pi x < 27^\circ$  or  $2\pi x$  lies between  $55^\circ$  and  $99^\circ$ .
6. ( $1123$ ) is not less than ( $1231$ ) or much more than ( $12\bar{3}1$ ) ;  $2\pi x$  lies between  $22^\circ$  and  $26^\circ$ , or  $77^\circ$  and  $107^\circ$ .

7. (1230) is very much stronger than (1123);  
 $2\pi x$  lies between  $46^\circ$  and  $90^\circ$ .
8. (3030) is less than a quarter (1230);  
 $2\pi x$  lies between  $25^\circ$  and  $95^\circ$ , or  $149^\circ$  and  $173^\circ$ .
9. (3032) is greater than (1014);  
 $2\pi x < 90^\circ$  or  $2\pi x > 152^\circ$ .
10. (1340) almost disappears;  
 $2\pi x$  lies between  $24^\circ$  and  $40^\circ$ , or  $73^\circ$  and  $131^\circ$ .

Any value of  $x$  between  $76^\circ$  and  $90^\circ$  will satisfy all those conditions, so that systems 23 and 24 are possible structures for selenium.

Calculated values for I were obtained by substituting in equations (1) and (2) the values  $2\pi x = 80^\circ$  and  $f(\theta) = \text{cosec}^2 \theta$ . Table II., Column V. gives the corresponding order of intensity for comparison with Column III. It is clear that the observed intensities fall off much more rapidly than those calculated from equations (1) and (2); this must mean that  $f(\theta)$  has some other value than  $\text{cosec}^2 \theta$ . The theoretical expression deduced by Darwin\* for the powder method gives this factor as

$$\frac{1 + \cos^2 2\theta}{\sin \theta} e^{-B \sin^2 \theta} F,$$

where B is a constant, and F is an unknown function which expresses the effect of electron distribution on the intensity of reflexion. In the present case, it is also necessary to bring in a factor to allow for the greater diffusion of the reflected beam in directions at right angles to the incident beam than in other directions†, so that the expression becomes

$$f(\theta) = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} e^{-B \sin^2 \theta} F. \quad (3)$$

It is impossible as yet to give any value to the factor F in the case of selenium. The only possible method of approach is therefore to find an entirely empirical expression for  $f(\theta)$  which agrees with the observed facts and involves no assumptions as to the nature of the function F. Equation (3) suggests several empirical formulæ, of which the following has been found to work best:—

$$f(\theta) = \frac{e^{-B \sin^2 \theta}}{\sin^2 \theta} \quad (4)$$

\* C. G. Darwin, *Phil. Mag.* xliii. p. 800, §§ 4 & 10 (May 1922).

† Compare J. M. Bijvoet and A. Karssen, *K. Akad. Wet. Amsterdam*, xxv. p. 17 (1922).



If we introduce a factor  $(1 + \cos^2 2\theta)$  into the expression, the intensity does not fall off sufficiently rapidly for  $\theta > 45^\circ$ . On the other hand, an expression of the form

$$f(\theta) = \frac{e^{-B \sin^2 \theta}}{\sin^2 \theta \cos \theta} \cdot \cdot \cdot \cdot (5)$$

fits the data practically as well as that given by equation (4), as is shown below.

Two values of  $B$  were substituted in equation (4), and the corresponding values of  $I$  were calculated from equations (1), (2), and (4). Giving  $B$  either of the values 2.72 and 3.40, the agreement with the observed intensities is good. It is useful, however, to try the effect of varying the value of  $x$  within a narrow region in the neighbourhood of  $2\pi x = 80^\circ$ . If we do so, we find the best agreement for  $2\pi x = 78^\circ$  and  $B = 3.4$ . For these values of  $x$  and  $B$ , Column VI. gives the calculated intensities and Column V. the order of intensity. If we take the difference between the observed and calculated orders for each line in turn, the arithmetic sum of these differences is the "Total Error" between the observed and calculated orders of intensity. This value is given in the bottom line of each column. Column VII. gives the actual values of the intensity calculated from equation (4), giving  $B$  the value 4.2. It differs very little from Column VI., so that equations (3) and (4) are almost equally applicable. Table III. gives the "Total Error" for varying values of  $x$  and two different values of  $B$ .

TABLE III. (Selenium).

Total Error in Order of Intensity for varying values of  $B$  and  $x$ .

Parameter ( $2\pi x$ ).	$70^\circ$ .	$75^\circ$ .	$78^\circ$ .	$80^\circ$ .	$85^\circ$ .	$90^\circ$ .
$B=0$ .....	...	...	...	41	...	...
$B=2.72$ .....	20	18	14	14	16	24
$B=3.40$ .....	20	12	10	12	20	24

To sum up, the observed order of intensity of reflexion is consistent with a value of the parameter  $2\pi x = 78^\circ$ .

## B. TELLURIUM.

### 5. Evaluation of the Parameter.

Tellurium only forms one crystalline modification. It has a density of 6.235 (Kahlbaum)\*, 6.338 (Beljankin)†. It is trigonal, being isomorphous with metallic selenium. The commonest forms are  $\{100\}$  and  $\{211\}$ . The angle

\* Kahlbaum, *Zeitschr. f. anorg. Chem.* xxix. p. 289 (1902).

† *Jour. Phy. Chim. Russ.* xxxiii. p. 670 (1901).

between the rhombohedral axes  $\alpha = 86^\circ 47'$ , which corresponds with an axial ratio  $a:c=1:1.3298$  (G. Rose)\*. Cleavage occurs most readily along (211), and less readily along (111).

Several photographs were taken, using different specimens of tellurium, with the results tabulated in Table IV.

TABLE IV.

I. $\frac{d}{n}$ (Obs.) $\times 10^{-3}$ cm.	II. $\frac{d}{n}$ (Calc.) $\times 10^{-3}$ cm.	III. Reflecting Planes.	Order of Intensity.		
			IV. Observed.	V. Calculated.	
				B=0.	B=2.0.
	5.91	0001	...	...	...
3.845	3.850	1010	16	19	14
3.220	3.224	1011	1	1	1
	2.957	0002	...	...	...
2.344	2.342	1012	2	2	2
2.219	2.222	1120	3	5	3
2.078	2.077	1121	12	16	13
1.968	1.972	0003	11	13	12
	1.925	2020	...	21	20
1.830	1.831	2021	5	7	5
1.765	{ 1.778	1122 }	15	15	15
	{ 1.754	1013 }			
1.614	1.612	2022	7	10	7
	1.478	0004	...	...	...
1.464	{ 1.474	1123 }	6	3	4
	{ 1.453	2130 }			
1.410	1.412	2131	9	9	9
1.375	{ 1.380	1014 }	9	11	11
	{ 1.378	2023 }			
1.308	1.307	2122 }	13	8	10
1.287	1.283	3030 }			
1.255	1.252	3031	14	17	16
	1.230	1124	...	22	21
	1.182	0005	...	...	...
1.172	{ 1.177	3032 }	4	6	6
	{ 1.172	2024 }			
	{ 1.170	2133 }			
1.131	1.130	1015	16	14	17
	1.111	2240	...	20	22
1.092	1.092	2241	18	18	19
1.075	{ 1.075	3033 }	19	12	18
	{ 1.068	3140 }			
1.051	1.050	3141			
1.038	{ 1.042	1125 }	8	4	8
	{ 1.040	2242 }			
	{ 1.037	2134 }			
Total Error .....				42	16

\* Pogg. *Ann. d. Phys.* lxxvii. p. 146 (1849).

Column I. gives the observed spacing, the mean values obtained from two films. These fit quite well on Hull's graph for a simple triangular lattice of axial ratio 1.33. The corresponding (hexagonal) indices are given in Column III. Assuming that the atomic weight is 127.5 and the density 6.3, it follows, as in the case of selenium, that there are three atoms associated with each point of the lattice. The calculated spacings after allowing for a slight systematic divergence are given in Column II. The corresponding value of the density is 6.25, and the length of the side of the base of a unit cell  $a=4.445 \text{ \AA}$ . This is in concordance with the results of Miss M. K. Slattery\*, who found that the structure of tellurium was based on a triangular lattice of axial ratio  $c:a=1.33$  and  $a=4.44 \text{ \AA}$ , three atoms being associated with each lattice point.

On comparing Columns I. and II. it is apparent that a number of lines are entirely missing. This is due to two causes: the films were not so clear as those of selenium, so that the weakest lines did not show up; but the peculiarities of the structure are also partially responsible. The complete disappearance of (0001) and (0002) offers us the same choice of structure as in the case of selenium. It is interesting that now the (0003) reflexion stands out clearly and is not masked by its coincidence with another line as with selenium. Similar arguments to those used for selenium show that we can reject any other type of structure but Sohncke's point-systems Nos. 19 and 20, and 23 and 24.

The observed orders of intensity are shown in Column IV. and are the mean from three films. In order to test systems 19 and 20 we endeavour to find a value for  $x$ , the indeterminate parameter which is reconcilable with the observed intensities. It must fulfil the conditions:—

1. Since (1010) is weak;  $2\pi x=180^\circ$ .
2. (2020) invisible;  $2\pi x=90^\circ$ .
3. (1011) is very strong;  $2\pi x=180^\circ$ .
4. (2021) very strong;  $2\pi x=90^\circ$ .
5. (3031) much weaker than (2021) but by no means disappears;  $2\pi x=75^\circ-150^\circ$  fulfils the first condition but (3031) vanishes for all the region around  $2\pi x=120^\circ$ .

Systems 19 and 20 clearly cannot afford solutions. As

\* *Loc. cit.*

with selenium systems 23 and 24 are the only possible arrangements. In confirmation of this we can find a possible value for  $x$  which will fulfil the following conditions:—

1.  $(10\bar{1}0)$  is weak ;  $2\pi x$  lies between  $93^\circ$  and  $165^\circ$ .
2.  $(1012)$  is almost equal to  $(11\bar{2}0)$  ; limits are  $85^\circ$ — $153^\circ$ .
3.  $(11\bar{2}0)$  greater than  $2 \times (11\bar{2}1)$  ; limits are  $94^\circ$ — $146^\circ$ .
4.  $(0003)$  greater than  $(1121)$  but less than  $2 \times (1121)$  ; limits are  $97^\circ$ — $104^\circ$  or  $143^\circ$ — $136^\circ$ .
5.  $(0003)$  greater than  $(10\bar{1}0)$  ; limits are  $94^\circ$ — $161^\circ$ .
6.  $(0003)$  greater than  $3 \times (20\bar{2}0)$  ; limits are  $45^\circ$ — $135^\circ$ .
7.  $(2022)$  greater than  $(2131)$  ;  $2\pi x$  lies below  $96^\circ$ .
8.  $(2131)$  not less than  $(10\bar{1}4)$  ;  $2\pi x$  lies below  $70^\circ$  or above  $89^\circ$ .
9.  $(22\bar{4}0)$  less than  $(224\bar{1})$  ; limits are  $17^\circ$ — $43^\circ$ ,  $77^\circ$ — $103^\circ$ , or  $137^\circ$ — $163^\circ$ .
10.  $(2\bar{2}41)$  greater than  $(30\bar{3}3)$  ; limits are  $2\pi x$  below  $98^\circ$  or above  $142^\circ$ .

A value of  $2\pi x$  about  $96^\circ$  or  $97^\circ$  appears quite satisfactory. As before,  $f(\theta)$  in equation (2) has been taken to be  $\text{cosec}^2 \theta$  and to minimize the possible error only neighbouring lines have been compared. All the experimental evidence, therefore, supports the choice of Nos. 23 and 24 for the structure of tellurium as well as selenium. Table IV., Column, V. gives the calculated orders of intensity obtained by the aid of equations (1) and (2), on the assumption that  $2\pi x = 100^\circ$ , and  $f(\theta) = \text{cosec}^2 \theta$ . A better agreement is obtained by the use of equation (4). Column VI. gives the order of intensity for  $B = 2.0$  and  $2\pi x = 97^\circ$ . These values give the best possible agreement with the observed intensities. The "Total Error" is still greater than in the case of selenium, but this is due to the inferiority of the films, in the case of tellurium. Table V. shows the "Total Error" for varying values of  $B$  and  $x$ .

TABLE V. (Tellurium).

Total Error in Order of Intensity for varying values of  $B$  and  $x$ .

Parameter ( $2\pi x$ ).	$90^\circ$ .	$93^\circ$ .	$95^\circ$ .	$97^\circ$ .	$100^\circ$ .	$105^\circ$ .
$B=0$ .....	...	...	...	...	42	...
$B=1.5$ .....	38	26	22	26	26	42
$B=2.0$ .....	40	34	20	16	34	46

The value of the variable parameter is therefore  $2\pi x = 97^\circ$ .

6. *The Structure of Selenium and Tellurium and its Relation to the Valency of the Elements.*

The results of the X-ray analysis show that the structure of these two elements corresponds with one of Sohncke's point systems, No. 23 or No. 24, whose projection is given in figs. 3 and 5, each figure referring to either system. No distinction has yet been made between the two systems. As far as X-ray analysis can be applied they are identical, and other methods must be employed to decide which is the actual structure. In both cases the atoms are arranged in threefold spirals around the trigonal axes, so that every third atom occupies the same position if projected on to a plane perpendicular to the trigonal axes. Such a structure may be either right-handed or left-handed. The two enantiomorphous systems are Nos. 23 and 24 respectively. It is possible that crystals of selenium and tellurium exist which correspond to each of the two systems. They would of course be indistinguishable by X-rays, but might be recognized by their outward form.

The structure of selenium is peculiar in that each spiral is so isolated from its neighbours. Every atom of selenium touches two atoms in the same spiral and four atoms in adjacent spirals. In the former case, the contact is much closer, the distance from centre to centre of adjacent atoms being 2.32 Å. The distance between atoms in different spirals is 3.49 Å. The difference between these two radii of combination is extremely large, and suggests a much greater cohesion between atoms in the same spiral than between those in different spirals. It is therefore possible that the crystals will tend to grow in the direction of the trigonal axis more readily than in other directions. Such an abnormal development might account for the occurrence of acicular crystals as described by Brown. Again, it is not unreasonable to suppose that owing to the weaker cohesion between neighbouring spirals, these may not always grow side by side to form a single perfect crystal; under certain conditions we may therefore get parallel growths, such as the lamellar crystals of selenium.

It is interesting to regard the structures of selenium and tellurium from a point of view which brings out their relationship to the structures of other non-metallic elements. If the value of the parameter was given by  $2\pi x = 120^\circ$ , selenium would have the structure of a simple rhombohedral lattice. The unit cell would be a rhombohedron containing one atom, the angle between rhombohedron edges being  $92^\circ 42'$  in the case of selenium and  $86^\circ 47'$  in the case

of tellurium. Thus the three interpenetrating lattices of selenium and tellurium fit together to form a structure which is almost simple cubic. In this respect selenium and tellurium resemble the elements of Group V. In the case of Group IV. the structure at first sight appears to be quite different as there is no distortion of the cubic lattice, but the only real difference is in the much greater value of the displacement from the simple cubic lattice. In general, the crystal structure of all elements of Groups IV., V., and VI. hitherto elucidated\* is a slightly distorted and internally displaced simple cubic lattice; the direction of displacement depends only on the valency of the elements.

In a simple cubic structure each atom has six equidistant neighbours. Since none of the atoms at present under consideration can present the same aspect to each of its neighbours, an atom of such a structure will be attracted unequally in different directions. This results in an internal displacement of the structure. The elements of Group VI. have two negative valencies, and each atom is in consequence drawn towards two of its neighbours. An atom of selenium or tellurium may therefore be displaced along any digonal axis of the simple cubic lattice. Actually the atoms of one crystal are only displaced in one of three directions, each perpendicular to the same trigonal axis, and making angles of  $120^\circ$  with the other two. Atoms constituting a triangular lattice with its trigonal axes perpendicular to the direction of displacement are shifted in the same direction. In the case of selenium the whole structure suffers a contraction, and in the case of tellurium an elongation, parallel to these trigonal axes. The trivalent atoms of Group V. are displaced towards three neighbours by movements along a trigonal axis, half the atoms, constituting a face centred lattice, being moved in each direction. The whole structure is again elongated parallel to this axis.

In the case of the tetravalent elements of Group IV. the displacement follows the same course. It is clearly impossible for an atom of a simple cubic structure to be shifted towards more than three of its six neighbours simultaneously. The displacement therefore proceeds as for a trivalent element, but continues beyond the point when each atom is co-planar with the three nearest atoms, so that it now approaches a fourth atom. Finally, each atom has four equidistant neighbours. Graphite does not conform to this type; each atom has three equidistant neighbours.

\* Lead and white tin are exceptions.

Debye \* and Hull † give two different arrangements, and which is the correct structure is still uncertain.

With this exception, in the normal crystalline forms of carbon, silicon, germanium, grey tin, arsenic, antimony, bismuth, selenium, and tellurium, electron sharing takes place until the outer shell of each atom has its full quota of electrons. In this way each atom of these elements is in close contact with as many neighbours as it has negative valencies. These elements are on the whole non-metallic in their chemical and physical properties. The exceptional structure of lead and white tin is consistent with their predominantly metallic characteristics. The accompanying plate (Pl. X.) shows models of the structures of arsenic and selenium. The atoms are represented by spheres in contact with each other. In order to represent close contact the spheres are cut away at the points of closest approach.

#### *Summary.*

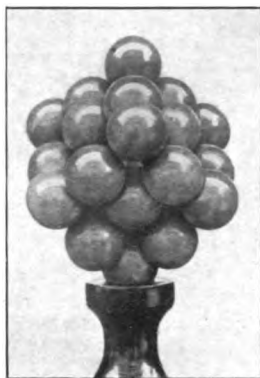
The structures of metallic selenium and of tellurium were determined by the powder method of X-ray crystal analysis; they may be regarded as simple rhombohedral structures with interaxial angles of almost  $90^\circ$ , in which each atom is slightly displaced towards two of the six adjacent atoms. The resulting structure is a threefold spiral, composed of three interpenetrating simple triangular lattices. It therefore allows of two enantiomorphous forms, which are indistinguishable by the methods of X-ray analysis.

The crystal structures of elements of Groups IV., V., and VI. differ from group to group in virtue of the difference in negative valency, which regulates the direction of displacement from the simple cubic structure which is the basis of the atomic arrangement. Elements in the same group differ in the extent of displacement, the heaviest atoms being the least shifted.

The author thanks Professor Bragg for his kind advice throughout the progress of this research, and again acknowledges his indebtedness to Dr. Brentano for his invaluable help and advice, especially in the initial stages of the work. Part of the apparatus used was purchased from money kindly given to the Physical Laboratory by the Government Grant Committee of the Royal Society, and by Messrs. Brunner Mond. The author is in receipt of a grant from the Board of Scientific and Industrial Research.

\* Debye, *Phys. Zeit.* xiii. p. 297 (1917).

† Hull, *Phys. Rev.* x. p. 682 (1917).



Arsenic.



Selenium.





LI. *An Experimental Study of Grating Errors and "Ghosts."*

By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University* \*.

[Plate XI.]

THE work to be described in the present paper was undertaken in the course of a study of the problem of making short-focus concave gratings for vacuum spectrographs. Since assuming charge of the Rowland dividing engines in the spring of 1923, I have investigated a number of the more or less obscure matters relating to diffraction gratings. The cause of the Lyman ghosts has been ascertained experimentally, and an attachment added to the engine which has abolished them completely. An optical method of studying the errors, periodic and otherwise, of gratings has been developed, which can be applied to any grating, either plane or concave. This method, while lacking some of the advantages of the method of cross-ruling, first suggested by Lord Rayleigh and employed by Rowland, is more sensitive than this, and will show the effect of two or three slightly misplaced lines, on a grating ruled with 15,000 lines to the inch. It has made possible the examination of the effects of stopping the machine for a few minutes during the process of ruling, throwing the thermostat out of action, opening the case and oiling the machine, etc. The method has, in addition, furnished experimental data which make it possible to visualize, so to speak, the manner in which the "ghosts" or spurious lines are produced, when a periodic error of ruling is present in the grating. The method consists of a photographic (or visual) determination of the intensity variations across the diffracted wave-front when the grating is illuminated with monochromatic light from a slit. If we examine the wave-front with a short-focus lens used as an eyepiece, at a distance of say 20 to 40 cm. from the grating we shall find the luminous field crossed by a multitude of vertical black lines arranged more or less in periodic groups. A brilliant source of light must be employed behind the slit. A quartz-mercury arc is best, and no lenses are employed. If a photographic plate is substituted for the eyepiece, we obtain a permanent record of the bands which can be studied at leisure. These bands can be observed on the wave-front almost up to the surface of the grating, becoming finer and more numerous as we approach the ruled surface.

\* Communicated by the Author.

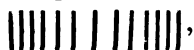
If a concave grating of short focus (say 1 metre radius of curvature) is examined in this manner, it will be found that, at a distance about half-way from the grating to the focus, the light has gathered itself into very bright vertical bars, the spaces between being quite black, the distance between the bars corresponding to the pitch of the screw of the dividing engine, reduced of course by the converging action of the grating. On moving the eyepiece back towards the focus these bars disappear gradually, the wave-front becoming nearly uniform in brilliancy. Still farther back the bars appear again, only to vanish once more as we near the focus. These same bars are seen with a plane grating used in conjunction with lenses in the usual manner.

On Pl. XI. figs. 1 to 7 reproductions are given of the photographic records obtained with a small concave grating of 1 metre radius, ruled with 15,000 lines to the inch. The slit was backed by a quartz-mercury arc, and the plates exposed at the recorded distances from the grating. A cell containing a dilute solution of copper chloride, placed close to the slit, cut off all radiations of shorter wave-length than 4358; the green and yellow lines are inoperative if ordinary plates are employed.

These photographs will doubtless come as a surprise to the reader who is accustomed to think of the diffracted wave-front as differing in no respect from ordinary wave-fronts of uniform amplitude—a condition that would obtain only in the case of a perfect grating, free from periodic errors of ruling.

The grating used in making these photographs had a periodic error somewhat in excess of those usually ruled. The reproductions have been enlarged three-fold from the original negatives, which were obtained by simply mounting a photographic plate in the path of the converging diffracted wave-front, at different distances from the grating. At 28 cm. and 60 cm. the bands are most distinct, the region between the luminous bars being almost black. At 55 cm. and 64 cm. they have practically disappeared, the illumination across the wave-front being nearly uniform.

These bright bars of light we may consider as formed in the following way. A single periodic error, such as results from a slight eccentricity of the large wheel with its 750 teeth, which turns the screw, gives us a grating in which the lines, instead of being equidistant, are arranged thus



this pattern repeating itself across the grating at intervals equal to the pitch of the screw. Now it is well known that

a grating in which the lines are ruled closer and closer together as we pass across its face has focal properties—that is, it exercises a converging or diverging action on the diffracted rays, according to whether we observe on the right or left of the central image. This action was first noticed by Cornu, and is fully treated in my 'Physical Optics,' the grating acting in a manner analogous to a zone-plate. Now in the present case we have this type of spacing, but reversed in direction at regular intervals; consequently the grating is made up of alternate linear elements, of which one set converges slightly, while the other diverges, the diffracted rays from the directions which they would have if the grating were perfect. The effect is more marked if the diffracted wave-front is already converging, as is the case with a concave grating. We can show the first system of bright bars by drawing a ray diagram for a grating of this type and its disappearance further on. Its subsequent reappearance involves an interference phenomenon, and cannot be shown very well by rays.

We will now take up the relation between these bars of light and the "ghosts" which accompany the spectrum lines when a periodic error is present in the grating. The very elementary explanation of the production of ghosts which I gave in 'Physical Optics,' is based on a type of periodic error which never occurs in practice, namely an extra line introduced at regular intervals. This can be accomplished experimentally by superposing a fine and a coarse grating. The spectrum lines given by the fine grating are accompanied by lateral spectra due to the coarse grating, forming the "ghosts." If we regard the coarse grating in the light of a periodic error, it is easy to visualize how the ghosts are produced. In practice, however, the error is a gradual change in the distance between the lines, and the analytical treatments are not very helpful in enabling us to form a picture of what is actually taking place. Our experiment shows us, however, that the wave-front at certain distances from the grating is broken up into vertical bars of light, separated by dark intervals of about the same width as that of the bright bars—in other words, not very different from an ordinary wave-front, *after it has passed through a number of parallel slits, in an opaque screen.* Following such a wave-front to the focus, we find a central image and lateral spectra. The "ghosts" correspond to these lateral spectra. We thus see that the periodic error has impressed upon the wave-front a condition similar to that produced by its passage through a coarse grating acting by opacity.

To test out this theory of the formation of the "ghosts," I tried intercepting the wave by a slit which could be made of such width as to transmit one, two, three, or more of the bright bars on the wave-front. We know, from the theory of the grating, that there are secondary maxima between the principal maxima to the number of  $n-2$ ,  $n$  being the number of lines in the grating. This was found to hold also in the present instance. If the slit transmitted four of the bright bars only, there were two faint maxima between the main line and each ghost to its right and left. It was found also that, at the second reappearance of the bright bars as we move back towards the focus, the number was always one less than the number transmitted by the wide slit. A somewhat similar effect is observed also when a converging wave-front of monochromatic light is passed through three or four narrow parallel slits, the phenomenon being related to the well-known periodic appearance and disappearance of the structure of a wire grating when viewed by transmission with monochromatic light at increasing distances. This treatment of the formation of ghosts enables us to see also why the ghosts of the first and third order are strong, while the second-order ones are very faint or absent. This is, at least, the case with all gratings ruled on the Rowland engines. From grating theory we know that if the widths of the transparent and opaque parts of a grating are equal, the spectra of even order are not present, since they lie in the directions of the diffraction minima of one of the transparent slits when operating alone. The vertical dark and light bars on the wave-front are of very nearly the same width; hence the ghosts of even order vanish. This point was verified by mounting a needle-point in coincidence with the point at which the second-order ghost would appear if present. The diffracted wave-front was now screened off with the exception of a single bright bar, and the needle-point was found to be exactly at the centre of one of the first lateral minima bordering the central maximum of the fringe system of Fraunhofer's first class, formed by a single slit.

As it sometimes happens that the ruling is interrupted by failure of the electric power, the method was used for a study of the effect of this accident on the ruling. The room in which the engine is operated is kept at a temperature constant to within  $1^{\circ}\text{C}$ . month after month, by a small gas-stove controlled by a toluene and mercury thermostat. The temperature within the glass case, in which the engine operates, is now kept constant to within  $0^{\circ}\cdot 1\text{C}$ . by electric heating, controlled also by a thermostat. The air in the room is kept

in constant circulation by an electric fan, and the products of combustion from the gas-stove are carried out of the room by a long stove-pipe, which distributes the heat of the stove over a wide area. A test ruling was made on a flat plate, and after the machine had been in operation for three hours, the motor was stopped for fifteen minutes, and then started again.

Fig. 13 (Pl. XI.) is a photographic record (enlarged three times) of the wave-front at a distance of 60 cm. from the grating, the black and white bar at the centre resulting from a local change in the ruling, due to the stopping of the machine. On examining the wave-front (green mercury light) with an eyepiece, it was found that this singularity could be followed right up to the grating, *i. e.* with the eyepiece practically focussed on the ruled surface. It appeared as a very fine vertical black thread running right across the ruling parallel to the lines. One would almost take oath that at least fifteen or twenty lines were missing altogether. On moving the eyepiece back, the line broadened and a faint black "satellite" split off from it, moving slowly across the grating in the direction in which the ruling had continued after the stopping of the machine.

It appeared important to determine, if possible, just what had happened to the grating at this point. I found that the black line could be seen if the grating was examined with a short-focus lens in the light of the third-order spectrum of a lighted window. Its position was indicated on the grating by a minute ink dot, which was then brought into the field of a microscope, illuminated with vertical light (green mercury line) from a transparent reflector just above the objective. To my surprise, instead of finding a narrow strip devoid of ruling as I expected, I found nothing peculiar in the ruling except that there were two lines somewhat closer together than the others.

By placing a horizontal slit in front of the reflector, I succeeded in so controlling the illumination that the ruling appeared as very narrow green lines separated by wide black intervals. A photograph obtained with a  $\frac{1}{2}$ -inch oil-immersion objective is reproduced on Pl. XI. fig. 12. The lines were ruled from right to left, the point at which the machine was stopped being indicated by an arrow. The next line ruled is a little closer to its right-hand neighbour than it should be, after which the grating space is slightly greater than the normal for several lines, to make up for the narrow interval, the lines coming into their correct position again presently. This was shown by measuring the photograph

on a dividing engine. To explain this we must suppose that on stopping the engine the carriage moves back a little, so that the next advance by the turn of the screw does not bring it to its correct position. A possible explanation may be that during the fifteen minutes of repose, the oil film between the screw and the nut was squeezed out, and since the nut is pushed forward by the front surface of the threads, this would cause the nut to retreat slightly when the oil film was removed. On starting the machine, oil is carried gradually into the spaces again, driving the nut and carriage forward, and giving a slightly increased spacing over that caused by the turning of the screw. This explanation is the only one that I can think of, and it may be found quite out of accord with what is already known about lubrication.

When we remember that the grating is ruled with 15,000 lines to the inch, it seems remarkable that the slight displacement of half-a-dozen lines causes a local change of illumination that can be seen on the face of the grating, with a lens of 1 inch focus used as a hand magnifier. As a matter of fact, we probably see the black line not really on the surface of the grating, but at a little distance in front of it, where the effect has spread by diffraction.

I was interested in seeing whether this local error affected the resolving power of a small strip of the grating embracing it. A slit 1 mm. in width limited the wave coming from the collimator of a spectroscope. This, however, covered enough lines on the grating to resolve the yellow mercury lines; no change in the resolution could be detected between the region containing the local errors and the rest of the surface. This shows us, in a different way, that only a very few lines are out of place, and we may infer from this that stopping the machine, for a short time at least, ought not to impair the resolving power. Cross rulings, however, show that we ought not to begin ruling until after the machine has been running for two or three hours.

I have examined, by the wave-front method, three very fine plane gratings ruled by Dr. Anderson on the same machine some ten years ago. These gratings are probably the best that have ever been ruled; one has five inches of ruled surface (75,000 lines), the other two seven inches, or 105,000 lines. They all have very nearly, if not quite, their full theoretical resolving power, and the ghosts are very faint, due to Dr. Anderson's skill in so adjusting the machine that the periodic error of the screw was practically compensated by introducing a slight eccentricity of the toothed wheel. A photograph of the wave-front from

the five-inch grating is reproduced on Pl. XI. figs. 10-11, the upper figure natural size, the lower enlarged a little over three-fold. Here we see a systematic interruption of the regularity of ruling which occurs about every twelve turns of the screw. The lower figure shows the region between two of these dark bars, and indicates how the wave-front is torn to pieces by errors of spacing, even in the case of a very perfect grating. Comparison of figs. 11 and 13 would lead one to infer that the machine had been stopped twice each day during the ruling, but this is hardly likely. It will be noticed that the dark bars are not exactly equidistant, as they would be if they were due to two periodic errors getting in step at regular intervals.

We will now take up the question of the "Lyman ghosts."

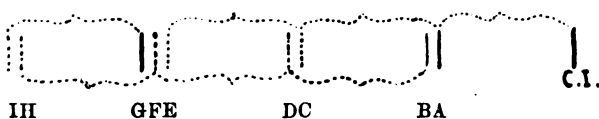
### *The Lyman Ghost.*

As is well known, periodic errors of ruling produce spurious lines or "ghosts" of two types, the so-called Rowland ghosts, first described by Quincke, which are symmetrically spaced to the right and left of, and close to, the strong lines of the spectrum, and another type, first observed and studied by Professor Lyman of Harvard University. These latter are more troublesome, as they are distributed at wide intervals, filling up the region between the central image and the first-order spectrum, and hence mingling with the lines of the spectrum investigated with vacuum spectrographs. Three papers appeared in the 'Journal of the Optical Society of America' for 1922 dealing with these ghosts, an experimental study by Meggers and Kiess, an analytical treatment by Runge, and a discussion of the sources of periodic errors of ruling engines by Anderson. As it appeared from these papers that two periodicities, in addition to the normal periodic error (which has a period equal to the pitch of the screw), were required for their production, and as one of these periodicities showed variation from time to time on the same machine, it was first necessary to determine their value at the present time. The slit of the vacuum spectrograph was illuminated by monochromatic light obtained from a cadmium spark by a quartz spectroscope. The instrument was not exhausted, and the concave grating of one metre radius was so adjusted that the central image fell just within the edge of the plate. Exposures of half an hour were given, ordinary plates being employed.



The Lyman ghosts appeared as in fig. 1.

Fig. 1.



On measuring the distances of these lines (which are all formed by light of a single wave-length) from the central image, it was found that the distances from C.I. to A, from A to C, and from C to E (E very faint) were equal. A, C, and E can thus be considered as first-, second-, and third-order spectra produced by the smaller periodicity. This was found to correspond to five lines of the grating, as in the cases considered in the papers referred to. The distance between A and B and between other adjacent lines of the groups gave a periodicity equal to 88 lines of the grating.

If we compare these ghosts with the Rowland ghosts as ordinarily found, we observe this difference. The latter are very faint and are symmetrical about the strong spectral lines of different orders. If, now, we try to picture the formation of the Lyman ghosts in the same way, we might expect the periodicity of five grating lines to produce strong spectral lines of order 1, 2, 3, etc., accompanied by fainter companions (analogous to the Rowland ghosts) due to the 88-line periodicity. This is not the case, however, as is seen from fig. 1, in which constant distances between lines are indicated by brackets. We should have a very similar condition if, in a system of spectra of various orders (of monochromatic light), we considered that the Rowland ghosts to the right of the main lines gradually died out as we ascended to higher orders, while those to the left increased in intensity until they surpassed the intensity of the main lines, which also die out in their turn. Rowland showed that similar effects were obtained with gratings ruled on the machine before the errors had been ground out of the screw, the ghosts often being stronger than the main lines.

Having determined the two periodicities responsible for the ghosts, a search for their source was made. Anderson had suggested that the five-line periodicity was accounted for by the circumstance that the driving-belt made two revolutions for every 5+ cycles of the machine, a distortion of the

whole machine resulting from the passage of thicker portions of the belt over the pulleys.

To study this matter in detail, a white mark was made on the large driving-pulley of the machine and another white mark on the belt, the two marks being in coincidence. The engine was then started. After one revolution of the belt, the pulley had made 2.5 revolutions, and the mark on the belt met the pulley on the side opposite to the white mark. After another revolution of the belt, the two marks came nearly, but *not quite* into coincidence. With each further double revolution of the belt, the marks drifted further apart, coming into coincidence again after 87 revolutions of the pulley. Since one line is ruled for every revolution of this pulley, we see at once that both periodicities are accounted for: the five-line one corresponds to the circumstance that a given point (say a thicker portion) of the belt is somewhere on a specified semicircumference of the pulley once in every 5 + revolutions; the 87-line one to the circumstance that the given point of the belt engages the same spot on the pulley once in every 87 revolutions. It follows from this that a coincidence of a thick spot on the belt with the very small motor pulley at the moment when the screw is advancing the carriage, will also occur once in every 87 cycles of the machine. The five-line periodicity suggests a slight eccentricity of the large driving-pulley.

In a paper on the vacuum spectrograph (Phil. Mag., Nov. 1923) I stated that the Lyman ghosts appeared to be developed with greater intensity with ultra-violet light of very short wave-length, since they were obtained with a five-minute exposure with the spark, while the mercury arc, screened with a filter of nickel glass (transparent to 3663), gave no trace of them, even with an exposure of half an hour. Their failure to appear in the latter case, I have since found was due to the fact that with the arc the wide cone of light entering the slit was in part diffused back to the plate by the inner wall of the spectrograph, fogging the plate, and prevented the faint ghosts from registering. By diaphragming the quartz-mercury arc so that the cone barely filled the grating, a profusion of ghosts appeared. The region between wave-lengths 700 and 1500 Ångströms is reproduced on Pl. XI. fig. 14 *b*. In coincidence with this spectrogram is another (*c*) made with the filter of nickel glass, which transmits only the mercury triplet 3650-3654-3663.

These are four-fold enlargements of the original negatives. The central image lies to the left, at a distance about equal

to the length of the spectrum reproduced. The approximate wave-lengths of real lines of the first-order spectrum, occupying the positions of the mercury triplet ghosts, are 730 Å.U. and 1460 Å.U. Time of exposure to quartz Hg arc,  $\frac{1}{2}$  hour. It was found that if a longer driving-belt was used, the slack being taken up by an idle pulley, the ghosts appeared in totally different positions, the spectrum of the ghosts of the total radiation of the mercury arc bearing no resemblance to the one reproduced, as was to be expected.

The method of driving the machine was now modified in the following way:—A pulley of the same size as the driving-pulley of the engine was mounted close to the latter on a separate support, the two being attached or “coupled” by means of six very thin rubber bands, attached to projecting studs on the two pulleys. This is essentially the same method which I devised for driving a 20-inch mercury reflecting telescope (*Astrophys. Journ.*, March 1909).

A grating ruled under these conditions was exposed for two hours in the spectrograph, the photograph showing only a very faint continuous band with no trace of the ghosts. Another grating, ruled under similar conditions, which showed traces of diffused light between the central image and the first-order spectrum when examined with the eye in sunlight, gave, with an exposure of one half hour in the spectrograph to the quartz Hg arc, a band made up of some 1500 very fine faint lines, so close together that it is very doubtful if any trace of them will appear in the reproduction (Pl. XI. fig. 14*a*). This grating is of the type usually described as “scratchy,” from the circumstance that the diffused light comes from narrow linear areas distributed in a quite irregular manner. I have not as yet determined positively the cause of this phenomenon, which is usually attributed to a breaking-down of the ruling edge of the diamond.

Photographs were made of the wave-fronts from two 1-metre concave gratings—one ruled with the elastic drive, and the other before the attachment had been applied. These are reproduced on Pl. XI. figs. 8 and 9, the former made with the grating free from Lyman ghosts. The latter shows apparently the combined effect of the engine periodicity and the ones introduced by the belt.

*Metallized Glass Concave Gratings.*

The continuous use of a concave grating in a vacuum spectrograph has been found by Millikan and others to result in a deterioration of the surface caused by products of the electric discharge.

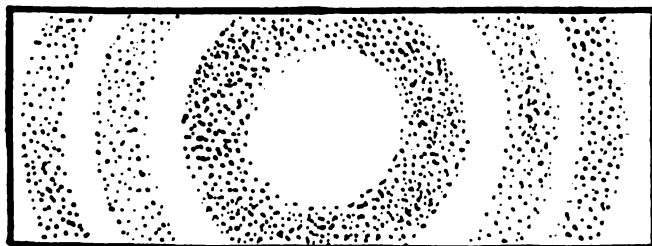
Millikan has stated that it was necessary to rule a new grating every few days for work in the region of the extremely short waves.

To overcome this difficulty, I propose to rule concave gratings on glass, etch them by the method which I described in the *Phil. Mag.* for Dec. 1906, and then deposit a metallic film on them. The difficulty in ruling glass gratings is due to the breaking-down of the diamond edge. If the pressure is *very* light, this does not happen, but no trace of the grating can be seen, or at most a spectrum so faint as to be almost invisible. Etching with very dilute hydrofluoric acid for a minute or less gives us a grating yielding spectra of great brilliancy. I have already etched a  $\frac{1}{2}$ -metre concave grating ruled on glass which looks very promising. This grating, when coated with a suitable metallic film by cathode discharge, should prove equal or superior to the ones ruled on speculum metal. When tarnished, they can be cleaned with acid, and given a fresh film of metal. Experiments along these lines will be taken up in the autumn.

*Target Pattern.*

Short-focus concave gratings, when examined by reflected light, especially in the higher orders of spectra, exhibit a circular target pattern similar to fig. 2.

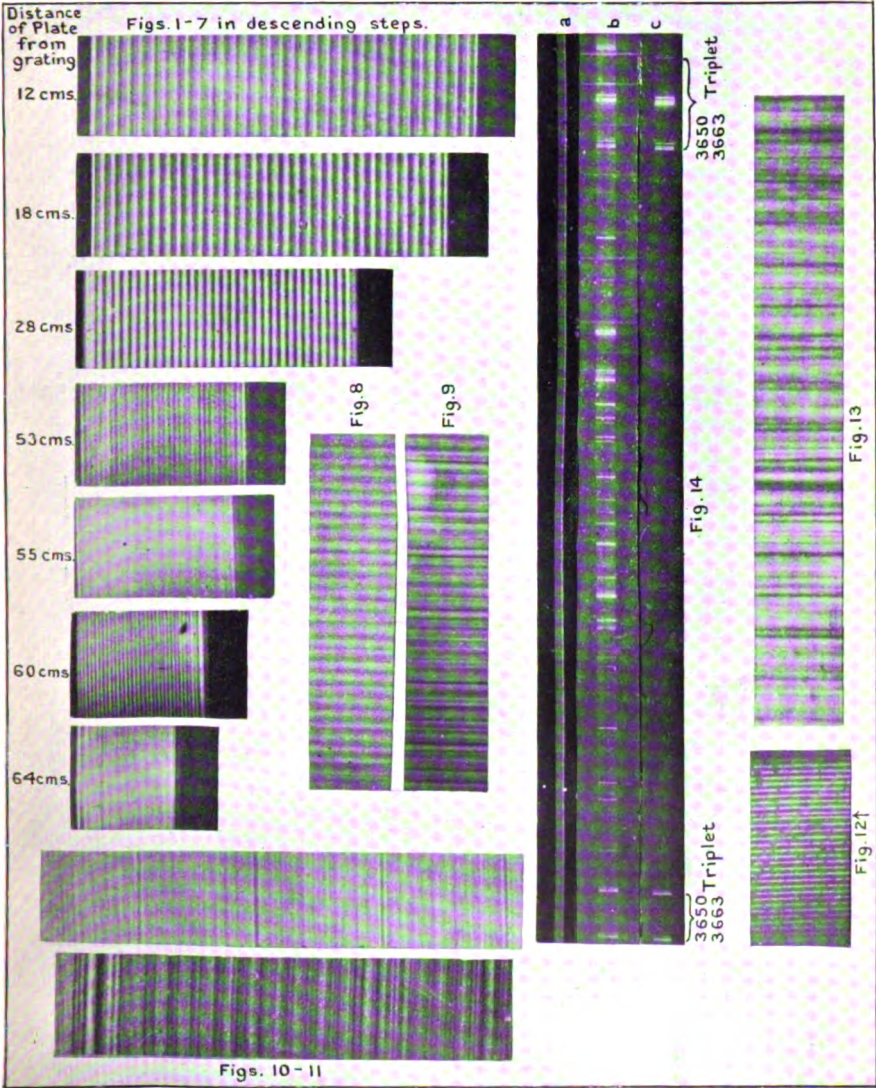
Fig. 2.



If monochromatic light is employed the rings are alternately bright and dark, while white light gives coloured rings, the even rings being red, the odds ones green, for example.

These rings are interesting as showing how the intensity distribution among the various orders varies with the part of the diamond edge used for the ruling. The ruling is done with one of the natural *curved* edges peculiar to the diamond, the edge being set parallel to the direction of the ruling. The diamond is mounted at the end of a horizontal lever ; consequently the *point* on the curved edge which comes in contact with the speculum plate varies with the distance through which the diamond drops before meeting the surface. With a plane grating, sloping uphill slightly in the direction in which the diamond moves when ruling a line, the diamond will be raised by degrees as it draws its line, and the point of contact will travel a trifle along the edge. A grating ruled under such conditions will have, say, the third order bright along one edge, and the fourth order bright along the other, due to the fact that different points on the curved edge of the diamond rule grooves of different form. In the case of a concave grating the diamond falls and rises as each line is drawn ; consequently the form of the groove varies along each line in the same manner. The locus of areas on the grating at which the ruling has been done with the same point on the curved edge of the diamond, is obviously a system of concentric circles. If the grating is not mounted level in the machine, with the centre of curvature at the middle point of the ruling, we have arches of colour instead of circles on the grating.

The concave gratings ruled on Lord Blythwood's machine at the National Physical Laboratory, at least the few which I have seen, show these patterns in a very irregular form, portions of hyperbolæ etc. which I cannot explain. Their cause is doubtless obvious to anyone familiar with the mechanism by which the diamond is lowered in this engine. The existence of this target pattern must be considered in connexion with the resolving power, since certain areas of the grating are inoperative, at least when working with higher orders than the first. The pattern figured is for a grating of 1 metre radius with  $3\frac{1}{2}$  inches of ruled surface, viewed in the fourth-order spectrum. In the first order the central circle covers about three-quarters of the grating.





LII. *On the Origin and Nature of the Long-range Particles observed with sources of Radium C.* By SIR E. RUTHERFORD, F.R.S., Cavendish Professor of Experimental Physics, and J. CHADWICK, Ph.D., Fellow of Gonville and Caius College, Cambridge\*.

§ 1. **D**URING the last few years much attention has been directed to an examination of the long-range particles which appear when a strong source of  $\alpha$ -rays bombards different materials. In this way, definite proof has been obtained that the nuclei of a number of elements are disintegrated by the bombardment of  $\alpha$ -particles with the emission of swift hydrogen nuclei.

In the early experiments which led to the discovery of the artificial disintegration of nitrogen, Rutherford † observed by the scintillation method that the passage of  $\alpha$ -particles from radium C through nitrogen and oxygen gave rise to some swift particles which had an equivalent range in air of about 9 cm., compared with that of 7 cm. for the colliding  $\alpha$ -particles. Just beyond the range of the  $\alpha$ -particles from radium C, the scintillations due to these particles are in general brighter than those due to H nuclei and more resemble those of  $\alpha$ -particles.

It may prove of some interest to give a brief account of the somewhat chequered history of subsequent attempts to fix the nature and origin of these long-range particles of 9 cm. range. It was natural at first to suppose that these scintillations were due to a new group of  $\alpha$ -particles arising from the source itself; but by examining the alteration of the range of the particles by the addition of thin sheets of aluminium and gold close to the source, it was concluded—erroneously as we shall see later—that the particles did not arise from the source but from the volume of the gas. If this were the case, the scintillations might be due to atoms of nitrogen and oxygen set in rapid motion by close collisions with the  $\alpha$ -particles, for the number and range of the particles were of about the magnitude to be anticipated on this point of view. To settle this point, experiments were made to measure the deflexion of the particles in a magnetic field. The mass of the particles could only be estimated by comparing their deflexion in a

\* Communicated by the Authors.

† Phil. Mag. xxxvii. p. 537 (1919).



magnetic field with that of other known particles which were similarly produced throughout the volume of the gas. For this purpose, the deflexion in a magnetic field of the particles of 9 cm. range was compared with that of H nuclei set in motion by the passage of  $\alpha$ -particles through a gas containing hydrogen. The experiments were difficult, as the number of particles under the experimental conditions was too small to give a sharply marked pencil of rays, but it was found that the particles, although less deflected than the H nuclei, were more deflected than was to be anticipated if they consisted of nitrogen or oxygen atoms carrying a single charge. It was estimated that the particles were probably atoms of mass about 3 carrying a double charge.

Some time later, measurements were made to determine the mass of the particles of range 11.5 cm. emitted by thorium C, which are given out in relatively greater numbers than the 9.3 cm. particles from radium C\*. Their deflexion in a magnetic field indicated that they were  $\alpha$ -rays of mass 4. This result raised the serious doubt whether the 9.3 cm. particles were not after all  $\alpha$ -rays of mass 4. This doubt was increased on finding that the relative number of these particles was independent of the nature of the gas surrounding the source of radium C; for example, within the experimental error the number was found to be the same in air, nitrogen, oxygen, carbon dioxide, sulphur dioxide, and chlorine, and the ranges in these gases were equivalent to that in air when due allowance was made for the stopping powers of the various gases.

Experiments were then made to find if definite proof could be obtained whether the particles were emitted by the source or whether they arose in the gas surrounding it. For this purpose the ranges of the particles were measured in air after passing through absorbing sheets of aluminium, silver, and gold of known stopping powers. It was found, however, that the imperfections of these foils due to holes, even when a large number of thin sheets were placed one behind the other, were too great to permit any definite conclusions to be drawn, and the experiments were abandoned.

Finally, however, by the use of a shadow method—described later in this paper—definite proof was obtained that the particles observed in oxygen had their origin in the source and not in the gas. The conclusions reached at this stage were briefly mentioned in an address † before the Chemical

\* Rutherford, *Phil. Mag.* xli. p. 570 (1921).

† Rutherford, *Journ. Chem. Soc.* 121. p. 413 (1922); 'Nature,' 109. p. 616 (1922).

Society, republished in 'Nature,' and are shown in the following quotation :—

"The next question which arises is whether any other particles besides that of hydrogen can be released by  $\alpha$ -ray bombardment. Some time ago, I found that when radium C was used as a source a small number of bright scintillations was observed, which had a maximum range in air of about 9 cm. It was natural at first to suppose that these were due to a new type of  $\alpha$ -rays from the radioactive source. The effect, however, of aluminium screens in reducing the range of these particles led me at first to believe that they were generated in the volume of the gases used, namely, nitrogen and oxygen. By comparing the bending of these rays in a magnetic field with those of H particles from hydrogen, I concluded that they must be atoms of mass about 3 carrying two positive charges. Later experiments have brought home to me the untrustworthiness of this method of fixing the source of the radiation on account of the marked variation in thickness of films of metal foil. Using a more direct and simpler method, I have recently convinced myself that, at any rate in the case of oxygen, the particles have their origin in the radioactive source and not in the volume of the surrounding gas. Under such conditions, the comparative method of estimating the mass of the particles is no longer trustworthy. While a large amount of experiment will be required to fix definitely the nature of the radiation, the general evidence indicates that it consists of particles of mass 4, which are projected from the source and represent a new mode of transformation of radium C."

At the time, attention was directed to experiments on the artificial disintegration of elements by  $\alpha$ -rays, and further investigation of the nature of the long-range particles was postponed to a more convenient season.

During the past year Bates and Rogers\*, in this laboratory, have made a detailed search for the presence of long-range particles from radium C, thorium C, actinium C, and polonium. In addition to the particles of 9.3 cm. range under discussion, they found evidence in radium C of other groups of particles of the  $\alpha$ -ray type, smaller in number and of ranges 11.2 and 13.3 cm. Similarly, groups of particles were observed from the other sources examined.

In view of the fact that the numbers of particles in these groups are of the same order as those to be expected if artificial disintegration were produced in the matter in the

\* Bates and Rogers, Proc. Roy. Soc. A, 105, p. 97 (1924).

path of the  $\alpha$ -rays, it has become a problem of immediate importance to settle definitely the origin and nature of these particles. We give in the present paper an account of a number of experiments which deal with this question. Our attention has been confined to the groups of long-range particles from radium C, since the active sources used in experiments on artificial disintegration usually consist of this material. We have examined carefully the number and range of the particles that appear when the  $\alpha$ -rays of radium C pass through different materials, viz., helium, oxygen, carbon dioxide, xenon, silica, and mica. We have examined also whether the observations are influenced by the mode of preparation of the source, and whether the particles appear in a vacuum. We have also devised experiments to fix the origin of the particles, and to determine accurately the mass and velocity of the particles by measuring their deflexion in a magnetic field.

As a result of these experiments, we have obtained convincing evidence that the long-range particles from radium C of 9.3 and 11.2 cm. range are  $\alpha$ -particles of mass 4 which have their origin in the source itself, and not in the surrounding matter. These particles, which appear whatever the material used to absorb the main beam of  $\alpha$ -rays, are to be regarded as two groups of swift  $\alpha$ -rays which are ejected from the product radium C, and probably represent new types of disintegration of that element.

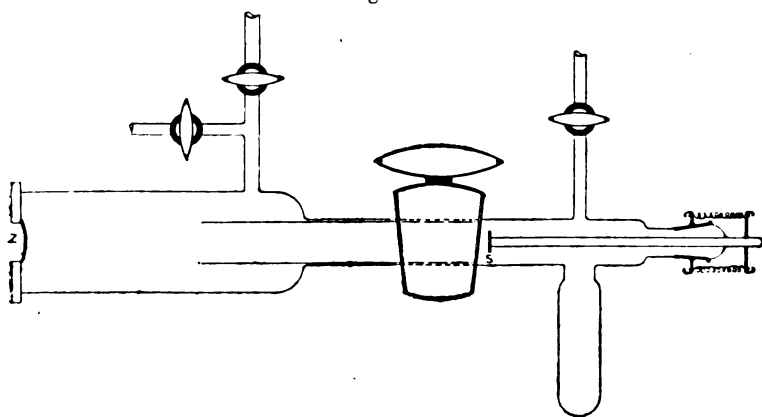
### § 2. *Examination of the Particles in different Gases.*

The earlier observations of one of us have shown that the particles of range 9.3 cm. are present when the  $\alpha$ -rays of radium C pass through nitrogen, oxygen, carbon dioxide, sulphur dioxide, chlorine, and boron trifluoride. We have extended these observations by comparing the number of particles obtained when the  $\alpha$ -rays were absorbed in helium with those obtained in oxygen, and examined the variation of the number of particles with increasing absorption in xenon, carbon dioxide, and some solids.

The comparison of the particles obtained in helium and in oxygen was carried out with the apparatus shown in fig. 1. It consisted of a long glass tube divided into two compartments by means of a tap of wide bore. The zinc-sulphide screen Z was fixed to the glass plate closing the end of the tube. It was protected from light emitted by the source or any material bombarded by the  $\alpha$ -rays by a very thin foil of aluminium. The source, S, of radium B + C was introduced

on the other side of the tap by means of a ground-glass joint. The parts of the tube close to the source were lined with brass in order to avoid the production of H particles from the materials of the glass. The distance between the source and screen was 35 cm. The apparatus was placed between the poles of a magnet to deflect the  $\beta$ -rays from the screen. After placing the source in position and evacuating the apparatus, purified helium was admitted to such a pressure (about 80 cm. of mercury) that the  $\alpha$ -particles of 7 cm. range in air were completely absorbed. It was found that scintillations still appeared on the screen to the number of 1.2 per minute per mg. activity of the source. When the

Fig. 1.



pressure of helium was increased to correspond to a range in air of 9.5 cm. most of these scintillations disappeared, the remainder amounting to about 0.2 per minute per mg.

By turning the tap in front of the source, the natural effect of the screen could be counted at any time during the experiment, and the presence of contamination immediately detected. This radioactive contamination, due sometimes to traces of emanation but more often to volatilization or removal of active deposit, is a source of great trouble in experiments of this kind, where the particles to be observed are an exceedingly small fraction of the number in the main group of  $\alpha$ -particles. It is our general experience that when contamination occurs the experiments must be abandoned.

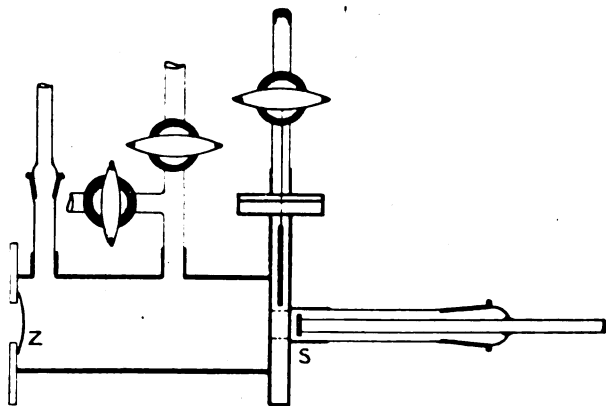
The helium was then pumped out and dry oxygen introduced to the appropriate pressure, and the long-range particles were again counted. The number observed was 1.0 per minute

per mg., decreasing to about 0.2 per minute per mg. when the pressure was raised to correspond to a range in air of 9.5 cm.

Within the accuracy of experiment, then, the number of long-range particles is the same in helium as in oxygen. The area of the screen observed in these experiments was approximately 40 sq. mm. and its efficiency about 70 per cent. The total number of long-range particles emitted by 1 mg. of radium C is therefore about 1100 per second. About one fifth to one sixth of these have ranges greater than 9.5 cm. of air.

Owing to the great stopping power of xenon for  $\alpha$ -particles, the experiments with this gas could be performed with a small distance between the source and screen, and the examination

Fig. 2.



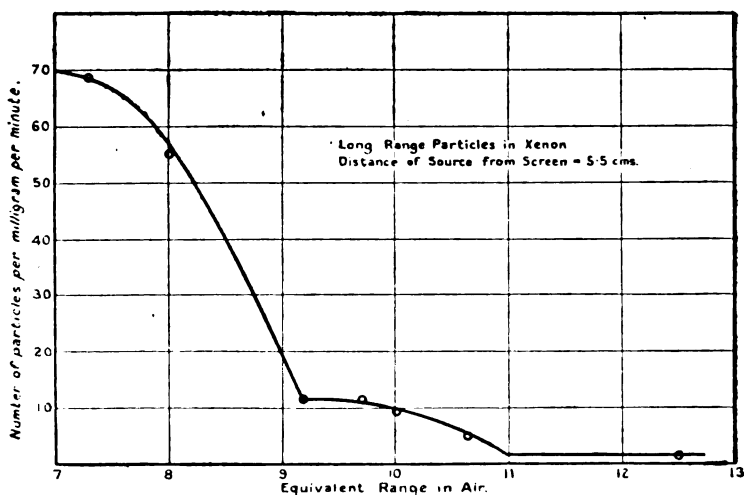
of the particles could be carried out with greater detail. The apparatus, shown in fig. 2, consisted of a brass tube 15 mm. in diameter, closed at one end by a glass plate carrying the ZnS screen, and having at the other end a brass slide which could be lowered in front of the source S by means of a winch. The distance between the source and screen was 5.5 cm. After introduction of the source, the apparatus was exhausted and then filled with xenon to a pressure of about 50 cm. of mercury. This was sufficient to absorb completely the  $\alpha$ -rays of 7 cm. range. The number of scintillations observed on the screen was then counted at various increased pressures of xenon up to atmospheric pressure. For the highest absorptions a mica sheet was placed in front of the screen. In such cases it was arranged that the main  $\alpha$ -particles were completely absorbed in xenon

and did not hit the mica, thus avoiding the production of extraneous H particles.

The occurrence of contamination could be at once detected by lowering the brass slide to cover the source. Some of the earlier experiments in xenon were completely vitiated by the presence of minute traces of radium emanation. As there is no satisfactory method of separating the emanation from xenon, the experiments had to be postponed until the emanation had decayed to a negligible amount.

The results of these experiments are shown in the curve of fig. 3, which gives the number of particles per minute

Fig. 3.



per mg. activity of the source at different absorptions, given in equivalent cm. of air. The curve shows clearly the existence of particles of two ranges, one just over 9 cm., the other about 11 cm. The number of particles of range greater than 11 cm. is very small, and there is no evidence of the group of 13.3 cm. range found by Bates and Rogers.

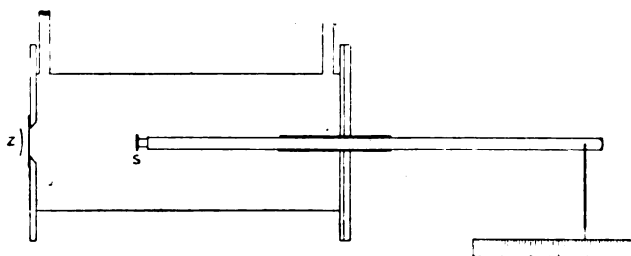
The area of the ZnS screen was 50 sq. mm., its efficiency about 70 per cent., and the distance from the source to the screen was 5.5 cm. We find therefore in xenon that 1 mg. of radium C emits about 1200 long-range particles per second, 1050 of a range of 9.3 cm. and 190 of a range of 11 cm.

A series of experiments was now carried out with the

source of  $\alpha$ -rays surrounded by carbon dioxide. The arrangement will be clear from the diagram of fig. 4. The source was placed in a brass box, the face of which was provided with a hole covered with a sheet of mica of 1.9 cm. stopping power. Sheets of mica of known air equivalent could be introduced in the path of the long-range particles just in front of the ZnS screen. The distance of the source from the screen could be varied at will and measured on a scale outside the box. A slow stream of carbon dioxide was passed through the box during the experiments.

We again observed the particles of 9.3 range and in the same numbers as in previous experiments, but the main point of this experiment was to determine the number of 11 cm. particles and to search closely for the presence of others of longer range. For this purpose, the source was fixed at a distance of 4.6 cm. from the mica sheet covering

Fig. 4.



the hole in the face of the box, so that the main  $\alpha$ -particles, of range 4.55 cm. in carbon dioxide, were completely absorbed in the gas.

The results of two typical experiments are shown in the curves of fig. 5. It will be seen that the number of 11 cm. particles is the same in both, the only difference being in the number of particles of longer range. There is no evidence whatever of a group of particles of range 13 cm. From these experiments we find that 1 mg. of radium C emits per second 180 particles of range 11.2 cm., in good agreement with the number found in xenon.

These particles were also examined when dry air was passed through the apparatus, the distance of the source being increased to 7.3 cm. The number of particles observed agreed with our previous results, but the observations were more difficult on account of the comparatively large number of particles which were present with ranges greater than 11 cm.

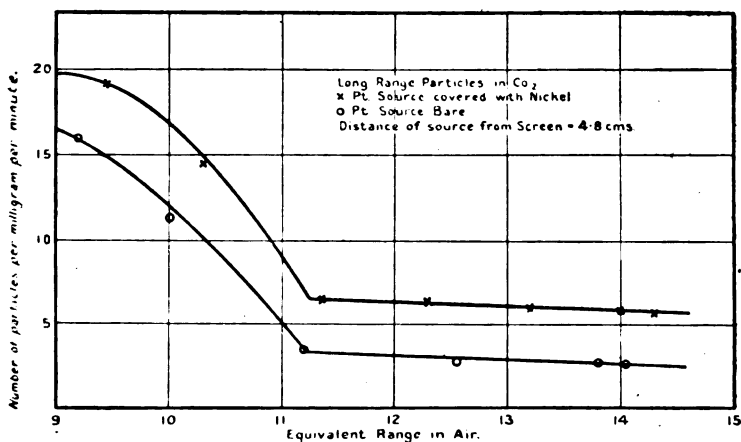
These were, of course, H particles due to the disintegration of nitrogen.

Further experiments were made in which the source of  $\alpha$ -rays was covered with a thin sheet of solid material of an air equivalent of a few centimetres, the remainder of the range of the  $\alpha$ -rays being absorbed in oxygen.

Using a thin sheet of silica of 2.3 cm. as absorbing material, we found that both the 9.3 and 11.2 cm. particles were present and in exactly the same numbers as in previous experiments. Very few particles were observed at greater ranges.

With a sheet of mica of 3.8 cm. stopping power, we observed the 9.3 cm. particles in their usual number. It was difficult

Fig. 5.



to measure accurately the number of 11 cm. particles against the background of H particles liberated from the mica by bombardment of the  $\alpha$ -particles. These amounted to about 30 per cent. of the total number of particles of range greater than 7 cm.

Observations taken with a piece of copper foil over the source showed the great danger of using metal foils in work of this kind. The piece of foil was selected carefully and was used with a source of small area (3 mm. diameter) in order to minimise the risk of imperfections. In spite of these precautions it was found that the foil varied greatly in thickness. It was difficult, owing to the imperfections of the foil, to fix the end of the range of the  $\alpha$ -rays with any accuracy, but it was evident that some parts of the foil had a stopping power of only 2.5 cm. of air, while the average



stopping power, deduced from its weight, was 3.8 cm. The result of these marked variations in thickness was to render the break between the main group of  $\alpha$ -rays and the long-range particles far less obvious. With a uniform foil or in a gas, as in the experiments recorded above, the end of the range of the  $\alpha$ -rays was extraordinarily definite and the presence of the long-range particles was brought out with great distinctness, while in this experiment with a copper foil there was merely a gradual diminution in the number of particles over a wide range of absorption. The failure of Fr. Dagmar Pettersson \* to detect the long-range particles must be explained by such an effect of the imperfections of the foils used for absorbing the main  $\alpha$ -rays.

The experiments described in this section show that when the  $\alpha$ -rays are absorbed in helium, oxygen, xenon, carbon dioxide, silica, and mica, the long-range particles are always present. They consist of two groups, of equivalent ranges 9.3 cm. and 11.2 cm. The number of the 9.3 cm. particles emitted per second by a source of 1. mg. radium C is about 1050, the number of the 11.2 cm. particles about 180.

We conclude from these results that the number and range, in equivalent cm. of air, of these long-range particles are independent of the material in which the  $\alpha$ -rays are absorbed.

### § 3. *Effect of different Methods of Preparation of the Source.*

The next point investigated was the influence of the method of preparing the source of radium active deposit on the number and range of the particles.

In the first place, observations with a source of pure radium C showed that it was this product, and not radium B, which gave rise to the long-range particles. On account of the greater ease in working, all other experiments were carried out with sources of radium B+C.

Usually the source of radium B+C was prepared by exposing a metal disk for about two hours to impure emanation. It was possible, though highly improbable, that the particles might be due to the disintegration of the metal or gases adsorbed in the metal. In most of the experiments described in the previous section the source was a platinum disk, which was heated to a high temperature in a vacuum furnace before exposure. Occasionally, brass and copper disks were used. The only difference noted was

\* Dagmar Pettersson, 'Nature,' p. 641, May 3, 1924.

in the number of particles of range greater than 11 cm., which was less for the platinum source than for the others.

Sometimes, in order to minimise the risk of contamination, a thin film of copper or nickel was deposited electrolytically on the source. This had no effect on the number or equivalent range of particles.

Spécial sources were then prepared in the following ways. In the first method, a platinum foil was taken to a high temperature *in vacuo* for some hours and then exposed to purified emanation. In the second method, a piece of platinum foil similarly heated was suspended in a vacuum above a layer of emanation condensed by means of liquid air on the end of a glass tube. The active deposit was obtained on the platinum by recoil. This method is similar to that devised by Pettersson\* for obtaining active sources.

In all these experiments the 9.3 cm. and the 11.2 cm. particles were always present and in the usual numbers, the only variation being in the number of particles observed at greater ranges (*cf.* the curves of fig. 5). The number of these was very small with a clean platinum source, particularly with sources prepared by the two later methods. They are probably due to traces of moisture in the material used to absorb the  $\alpha$ -rays, or to moisture or possibly nitrogen adsorbed on the surface of the source.

We find, then, that the numbers and ranges of the long-range particles are independent of the method of preparation of the active deposit or of the material on which it is obtained.

#### § 4. *The Origin of the Particles.*

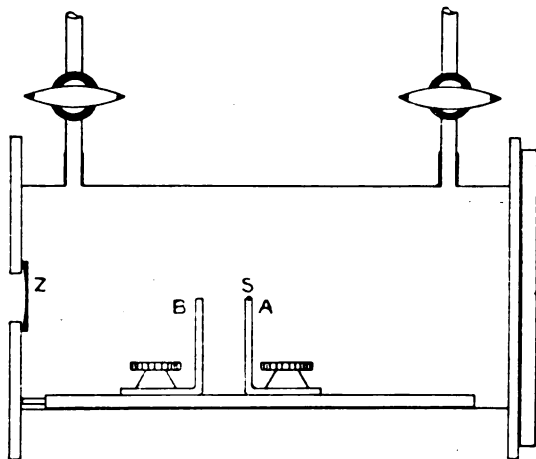
We shall now describe an experiment which shows that the long-range particles come from the source.

The apparatus is shown in fig. 6. The source, a platinum wire of .25 mm. diameter, was carried in slots at A, and a graphite edge was placed 1 cm. distant at B. The zinc-sulphide screen, Z, was 5 cm. distant from the source. Carbon dioxide was circulated slowly through the apparatus. When the pressure of the gas was reduced sufficiently to allow the main  $\alpha$ -rays to reach the screen, a sharp shadow of the graphite edge was formed. The position of the microscope was adjusted so that a cross-wire in the eyepiece coincided with this edge. The pressure of the gas was then restored to atmospheric, and the scintillations due to the long-range particles were observed. It was found that no

\* Pettersson, *Wien. Ber.* 132. p. 55 (1923).

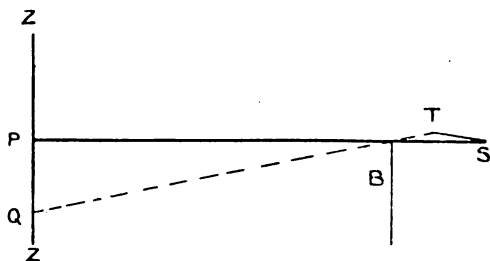
scintillations, except those due to the natural effect of the screen, occurred above the cross-wire, that is, below the edge of the shadow. This admits of two explanations.

Fig. 6.



Either the long-range particles are emitted from the source, or, if they arise in the gas, their direction of emission cannot make an angle of more than a few degrees with the direction of the impinging  $\alpha$ -particle. This is made clear by the diagram of fig. 7, in which P is the shadow of the edge B given

Fig. 7.



by a beam of  $\alpha$ -particles from the source S. If the long-range particles were produced in the gas and if their direction of emission made even a small angle with the direction, say ST,

of the colliding  $\alpha$ -particle, then scintillations would be observed on the screen below P, for example at Q.

Taken in conjunction with other evidence, this experiment provides a simple and direct proof that the long-range particles are emitted by the radioactive matter of the source.

### §5. *The Magnetic Deflexion of the Particles.*

In some unpublished experiments Bates and Rogers, by a method similar to that used by one of us for the same purpose, compared the magnetic deflexion of the 9.3 and 11.2 cm. particles with that shown under the same conditions by the  $\alpha$ -rays of thorium C of 8.6 cm. range. Within the limits of error of the experiment, the results obtained were consistent with the view that both sets of particles were  $\alpha$ -particles.

We have measured the magnetic deflexion of the 9.3 cm. particles by two methods.

In the first method, we used the arrangement described in the previous section, in which the particles pass through an atmosphere of carbon dioxide and throw a shadow of a graphite edge on the zinc-sulphide screen. If a strong magnetic field be applied at right angles to the path of the rays and to the plane of the diagram of fig. 6, the particles will be deflected and the shadow of the graphite edge will move downwards, say. On reversing the direction of the field, the shadow will move upwards. The distance between the two positions of the shadow gives a measure of the value of  $mv/e$  for the particles.

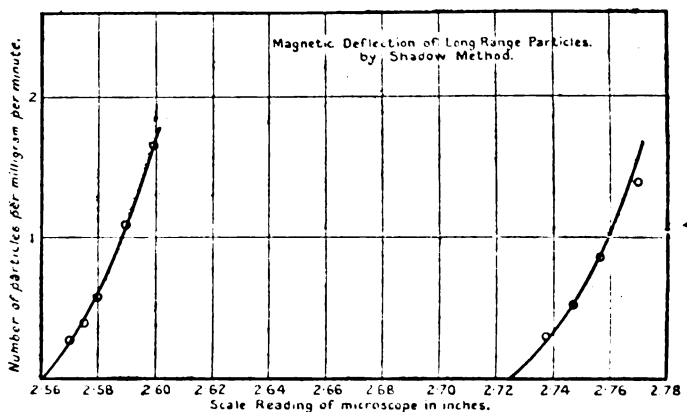
The apparatus was calibrated by observing the deflexion of the shadow cast by the  $\alpha$ -particles of range 8.6 cm. emitted from a strong source of thorium B + C. The number of scintillations was so great as to give a definite edge to the beam, and the cross-wire of the microscope could be adjusted on the edge with great accuracy. With a current of 6 amps. through the magnet coils the distance between the two positions of the edge was .173 inch or 4.39 mm.

The number of the 9.3 cm. particles was not sufficient to show at once the sharp edge of the shadow. For these particles, the microscope was set with the cross-wire close to the edge of the beam, and the number of particles appearing above the cross-wire was counted as the microscope was moved by successive small steps into the beam of particles.

The result of one experiment is shown in fig. 8. The ordinates give the numbers of particles counted above the cross-wire per mg. activity of the source for the different positions of the microscope given by the abscissæ. The point of intersection of the curve with the base-line gives the position of the edge of the shadow, and it is seen that this can be fixed with surprising accuracy.

A little consideration will show that the edge of the upper shadow is formed by the less deflected particles, the edge of the lower shadow by the more deflected particles. Thus only the readings of the upper edge are affected by the presence of the 11.2 cm. particles. This effect is not serious on account of the relatively small number of these particles.

Fig. 8.



The distance between the two positions of the edge found from the above experiment was .165 inch. In a second experiment, we found a value of .166 in., a rather better agreement than one would expect from the nature of the experiment.

Comparing this with the deflexion found for the  $\alpha$ -particles of thorium C, and allowing for the difference in range, we see that the long-range particles have very closely the same value of  $mv/e$  as  $\alpha$ -particles of the same range.

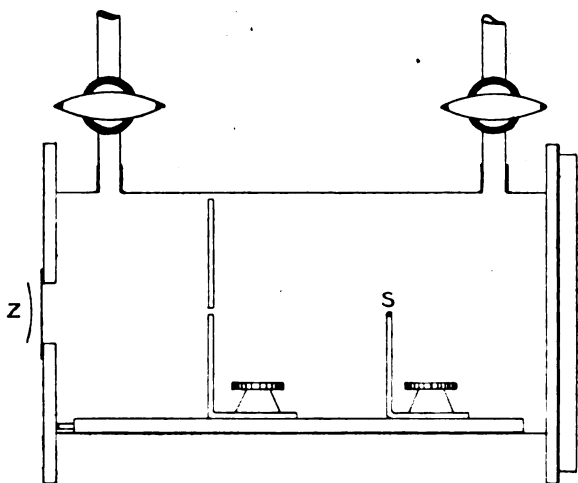
A further check can be obtained by measuring the magnetic field and calculating the deflexion which would be shown by an  $\alpha$ -ray of range 9.3 cm. under the experimental conditions, *i.e.*, taking into account the change of velocity along the path through the gas. In this way we

find a deflexion of 4.23 mm., compared with the deflexion of 4.20 mm. observed for the long-range particles.

We conclude, therefore, that the long-range particles of 9.3 cm. range are  $\alpha$ -particles.

The second arrangement for measuring the magnetic deflexion of the long-range particles is shown in fig. 9. It consists of a wire source of .25 mm. diameter and a slit of .5 mm. width contained in a narrow brass box. The box was evacuated during the experiments. The end of the box was closed by a brass plate containing a rectangular aperture 1 cm.  $\times$  1.5 cm., over which a mica sheet of 7.2 cm. air

Fig. 9.



equivalent was fixed. The ZnS screen was outside the box, and was fixed to the microscope, so that the same part of the screen was always observed. The distance from the source to the slit was 5 cm. and to the screen 10 cm. Under these conditions the width of the band of scintillations observed on the screen was 1.25 mm. The position of this band was observed when no magnetic field was applied and then with a field of about 12000 gauss, due to a current of 6 amps. through the magnet coils. A diaphragm of rectangular aperture and a central cross-wire were placed in the eyepiece of the microscope, giving a field of view 8 mm. in length and 1.54 mm. in width.

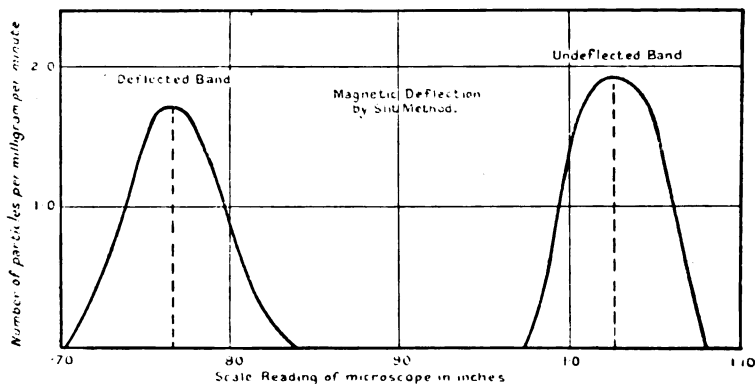
First, the deflexion of the  $\alpha$ -rays of 8.6 cm. range emitted

by thorium C was examined, using a source of 1 mg. of thorium B + C. This gave a band of scintillations with sharp edges on which the cross-wire could be easily adjusted. With the magnetic field due to a current of 6 amps. the band was deflected through a distance of  $\cdot 261$  in. or  $6\cdot 63$  mm. This experiment also enabled us to fix accurately the centre of the undeflected band.

The source of radium B + C was then placed in position and scintillations were counted as the microscope was moved over the deflected band of long-range particles. The main  $\alpha$ -rays of 7 cm. range were cut out by the mica. The position of the undeflected band was measured in a similar way.

The result of the experiment is shown in fig. 10. The

Fig. 10.



maximum of the deflected band is displaced by a distance of  $\cdot 259$  in. from the centre of the undeflected band. The deflexion calculated on the assumption that the 9.3 cm. particles are  $\alpha$ -particles is  $\cdot 254$  in., about 2 per cent. less. Under the circumstances this is a very fair agreement, for we must remember that besides the 9.3 cm. particles there are also present the group of 11.2 cm. particles, and some H particles produced in the mica sheet by the 7 cm.  $\alpha$ -rays. In other experiments we have found that the number of these H particles is about 30 per cent. of the number of 9.3 particles. The magnetic field used was not sufficiently strong to separate completely the bands of scintillations due to the 9.3 cm., the 11.2 cm., and these H particles, which latter will be produced where the 7 cm. particles strike the mica. It is clear, however, that the effect of these extraneous particles is to shift the maximum of the band towards the

side of greater deflexion, and a detailed calculation of the variation in number of the scintillations which should be observed at different parts of the band gives a result which agrees closely with experiment.

A further point is brought out in this experiment. If the 9.3 cm. particles were not emitted by the source but due to bombardment of atoms in the path of the  $\alpha$ -rays, then the deflected band should be found where the 7 cm. particles strike the mica, that is, its centre should be at .747 on our scale (*cf.* fig. 10). As this is not the case, we have a further proof that these particles are emitted by the source.

We may also compare the number of particles observed in this experiment, *i. e.* when all gases surrounding the source are removed, with the number we should expect from experiments in gases. Taking into account the fact that only one side of the wire source is effective and that of the total length of 9.5 mm., 2.5 mm. were shielded by the slots in which the wire is held, we find that the numbers correspond closely.

We conclude from these measurements of the magnetic deflexion of the 9.3 cm. particles that they are  $\alpha$ -particles emitted from the source and that their number is the same when the source is in a vacuum as when surrounded by a gas.

#### § 6. Summary.

In the series of experiments described in this paper we have obtained definite evidence about the nature and origin of the long-range particles which appear from a source of radium C. This evidence may be summarized as follows:—

- (1) The particles of 9.3 cm. range appear in equal amount in helium, oxygen, carbon dioxide, and xenon.

The same is true for the particles of 11.2 cm. range, though on account of the small number of these the evidence is not so definite.

The experiments with helium appear to us to give conclusive evidence against the hypothesis that the particles arise from disintegration of the gas through which the  $\alpha$ -particles pass. Whatever opinions may be held as to the stability of atomic nuclei, no one will lightly suppose that a helium nucleus is of no more than average stability.

We have found no evidence of the particles of 13.3 cm. range claimed by Bates and Rogers. The number of 11.2 cm. particles is also much less than they state. These discrepancies are probably due to the use in their experiments of absorbing foils of mica. This gives rise to comparatively large numbers of H particles and renders the detailed



investigation of the particles of greater range than the 9.3 cm. rays much more difficult.

- (2) Both sets of particles were observed, and in the same numbers as before, when sheets of silica and mica were placed immediately over the source.

Experiments with an absorbing foil of copper have shown the great danger of using metal foils in work of this kind.

- (3) The particles appear in the same number and with the same range in whatever way the source is prepared.
- (4) By a shadow method, we have shown that the particles come from the source, or, if produced in the gas, travel in the direction of the impinging  $\alpha$ -particle.
- (5) The deflexion of the particles in a magnetic field corresponds within a small experimental error with that to be expected if they are  $\alpha$ -particles emitted by the radioactive source.
- (6) The magnetic deflexion in a vacuum shows definitely that the particles of 9.3 cm. range are emitted by the source. The number of the 11.2 cm. particles is too small for the application of this test.
- (7) The particles of 9.3 cm. range appear in the usual number when the space surrounding the source is evacuated.

From this evidence there appears to us only one possible conclusion, namely, that the long-range particles are  $\alpha$ -particles arising from the disintegration of radium C. In the case of the 9.3 cm. particles the evidence is overwhelming. On account of the small number of the particles of 11.2 cm. range the experiments cannot be carried out in such detail and the results are less conclusive, but there is no reason to doubt that they are of the same nature. These two groups of  $\alpha$ -particles probably represent new types of disintegration of radium C, but any speculation about the mechanism which gives rise to them would be out of place in this paper, in which we have tried to confine ourselves to the narration of the bare experimental facts.

Our thanks are due to Mr. Hirst and Mr. Osgood for their assistance in counting, and to Mr. G. R. Crowe for his help in preparing the sources and arranging the experiments.

Cavendish Laboratory,  
July, 1924.

LIII. *On the Output of Radiation from the Quartz Mercury Arc during the Period after first striking.* By B. D. H. WATERS, B.Sc., *Physics Dept., Middlesex Hospital* \*.

**D**URING a series of observations on the time taken by a mercury arc to reach a steady state, certain variations of output were noticed during the first few minutes.

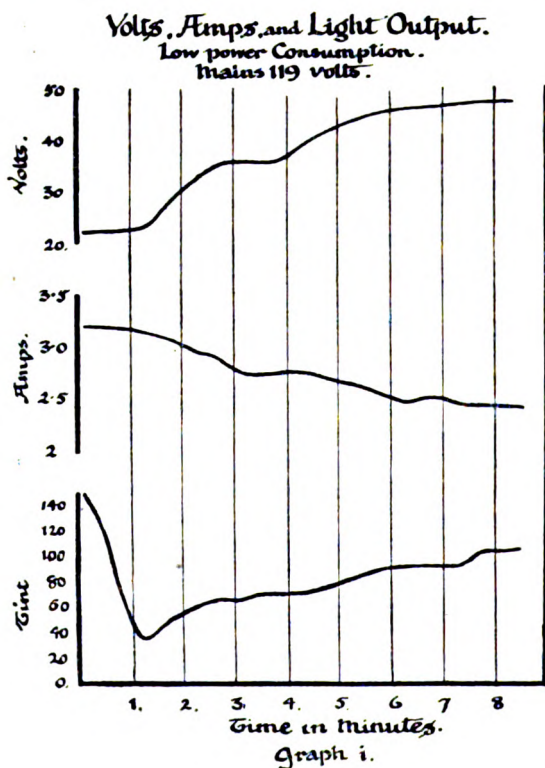
The rate of consumption of electrical energy by the lamp at any moment was measured by an ammeter placed in the circuit and a voltmeter across the lamp terminals, the current being drawn from a bank of accumulators to ensure steady supply conditions. The arc was then struck and readings of the instruments taken after 15 secs. and then at intervals of 30 secs. The output of light was measured by the tint obtained on a strip of gelatino-chloride printing paper (P.O.P.) exposed to the full radiation from the lamp behind an aperture. At the end of 30 secs. the strip was moved on sharply, any error introduced in the actual movement being much less than could be detected by the method of tint matching. In this way a series of tints was obtained, the depth of colour being a measure of the output during consecutive periods of 30 secs. It will be noticed that the reading of voltmeter and ammeter occurs at the mid point of each photographic exposure.

To obtain a relative figure expressing the depth of the tint the lamp was allowed to attain a steady state. When both instruments registered constant readings and the sensitive paper a constant tint, a series of standard tints was prepared on a piece of the same paper by exposing it for times ranging from 5 to 40 secs.

Each tint of an experimental series was then matched against the standard series and thus given a relative value. By this method the tints are expressed as a percentage of the tint corresponding to the final output, *i. e.* when the lamp has reached a steady state. An alternative method making use of a series of permanent standard tints made in water colours was tried, but the difficulty of colour matching and the additional error thus introduced confirmed the use of the simpler method described above. This method it will be noticed has also the advantage that any error due to variation in sensitivity and colour of one batch of printing paper from another is eliminated by using the same sheet for both exposures. The matching was done by the light of a 4-volt electric lamp kept at a constant distance.

\* Communicated by Prof. Sidney Ross, D.Sc.

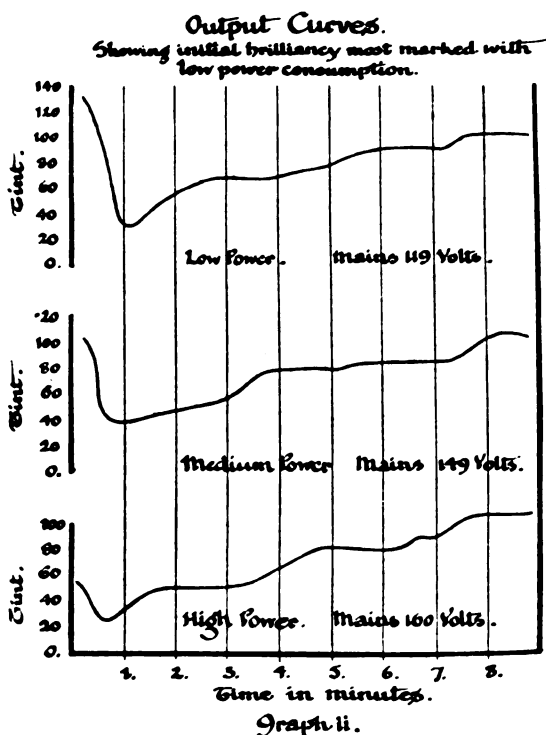
It was found that, whatever the experimental conditions of voltage and series resistance, the first tint was always deeper than those immediately following. This preliminary burst of light was followed by a fall to a minimum, and then a slow and rather jerky rise to a steady output which was attained in 10 to 15 minutes. The first effect is especially marked when the lamp is run at a low power consumption



(see Graph II.). In one experiment (see Table I.), when the lamp was running at its lowest possible voltage, the output recorded by the sensitive paper during the first half-minute fell to a quarter of that value in the period following next but one. It will also be noticed from the table that the lamp did not regain the original intensity, the initial tint being about 40 per cent. deeper than the final steady output. The fluctuations in voltage, current, and tint output are shown

in Graph I., and it will be noticed that during the period of the rapid change in the intensity of the radiation, the readings of both instruments are virtually steady. On the other hand, the irregular rise in voltage and corresponding fall in current are roughly reflected in the output curve.

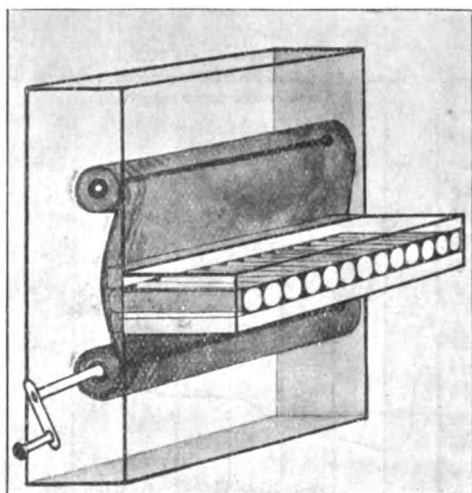
All these observations were made with the whole light from the arc. In order to discover whether the effect was confined to any particular part of the discharge, an apparatus



was constructed, a sketch of which is shown in fig. 1. This apparatus consisted essentially of 11 lengths of brass tubing, each 7.5 cm. long and 1 cm. diameter, placed side by side in a frame and fixed in the front of a light-tight box. Inside the box was a simple mechanism by which a wide strip of sensitive paper was wound off one small roller on to another in such a way that it was stretched across the farther ends of the tubes. In order to minimise reflexions the inside surfaces

of the tubes were given a mat black coating of lamp-black and turpentine. The apparatus was adjusted close up against the lamp, so that each tube received the light from a small section of the tube only. When this strip was exposed for consecutive 30-second intervals after striking the arc, the

Fig. 1.



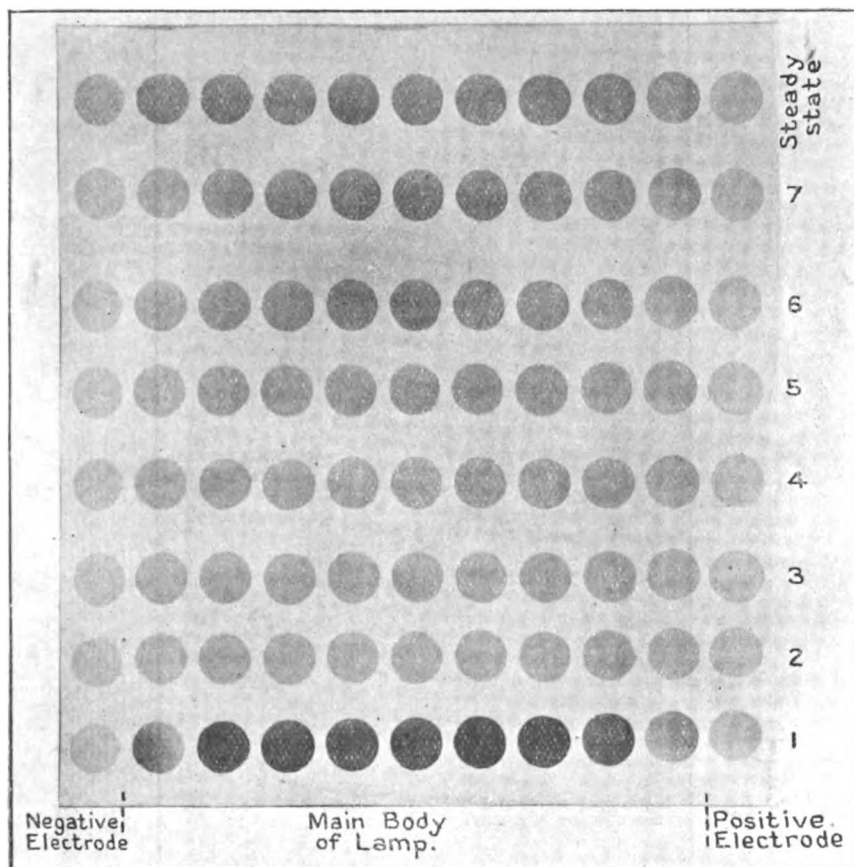
result shown in fig. 2 was obtained. The bottom line of tints is the first exposure. The first tube on the right was bearing on the positive electrode, the large spherical bulb which remains about half full of mercury. Owing to the low voltage at which the lamp was run, the discharge does not fill the bulb, which is, therefore, not very brilliant. The negative electrode is covered by the tube on the extreme left and the main body of the lamp by the nine central tubes. The print shown is typical of a number obtained in this way, and shows clearly that the initial brilliance is confined to the centre portion of the tube, there being no trace of it at either electrode.

A spectroscopic examination of the radiation was then made, using a Hilger quartz spectroscope and panchromatic plates. The same exposure period of half-a-minute was employed, the light being taken from the centre of the lamp only, making use of the apparatus described above. On each

*from the Quartz Mercury Arc after first striking.* 531

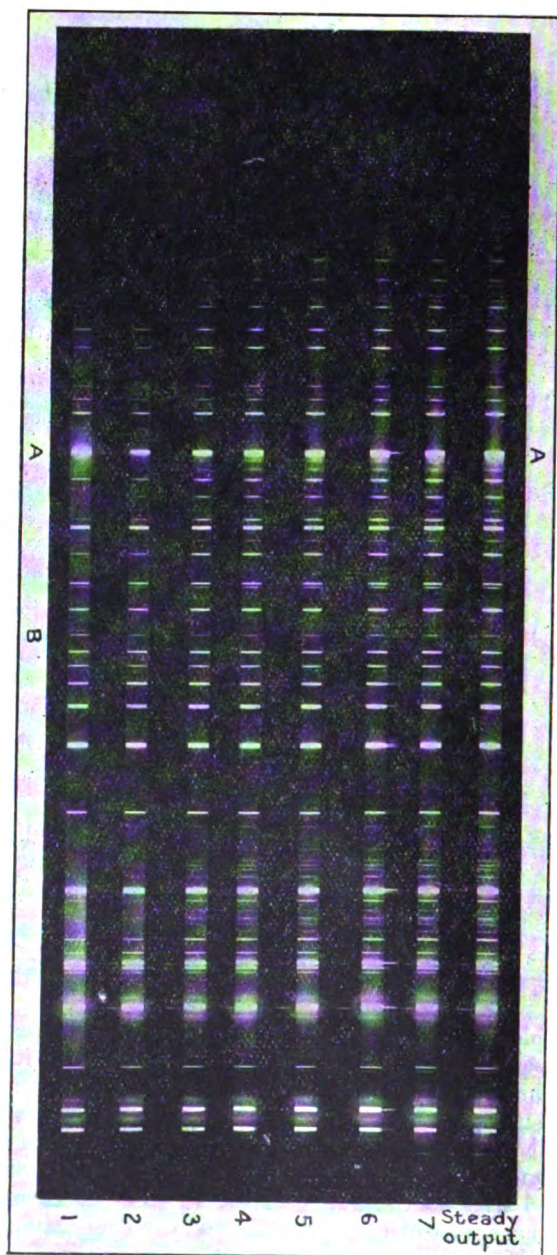
plate the spectrum of the steady radiation was also included for purposes of comparison.

Fig. 2.



A typical result is shown in fig. 3. The first spectrum is the lowest on the plate, and it will be seen that it is very much simpler than the top one which is the spectrum of the steady state. A number of the lesser lines do not appear at all until after a minute or more has elapsed. Some lines show, on the other hand, a marked maximum at the start, followed by a sharp drop, and then a steady increase. The less intense lines of this type fade away entirely and reappear

Fig. 3.



again. The most marked example is the line of wave-length ( $\lambda$  2536), which is marked A in the print. There can be little doubt that it is this line which is responsible for the effect under observation. It is interesting to note that in some earlier experiments this line was found to have by far the greatest photoelectric effect of all the lines of the mercury spectrum\*. The initial brilliance was somewhat exaggerated by the selectivity of the paper. It was found that this paper was sensitive throughout the whole range of the ultra-violet covered by the quartz spectrometer.

A print was made in the spectroscope directly on the paper by an exposure of over four hours, which showed that the yellow and green lines had little or no effect, whilst all the main lines in the ultra-violet were strongly marked. The selectivity of the printing paper thus accentuates any fluctuation in the ultra-violet region.

An attempt was made to record the fluctuations during periods of about 1 sec. A revolving shutter with a sector of  $180^\circ$  was used, but beyond confirming the fact that the intensity of  $\lambda$  2536 starts at a maximum value at the instant of striking the arc, nothing very conclusive could be obtained.

To measure any minor variation in intensity apparatus of precision would have been a necessity.

In order to summarise the evidence of the spectroscopic experiments, the lines may be divided into three groups. First, the lines which show a small but gradual increase of intensity as the lamp runs steady. Secondly, the lines which show an initial maximum followed by a drop and a steady rise. Thirdly, those which do not appear at all until an interval after the arc is struck. One minor line cannot be placed under any of these categories. This line ( $\lambda$  2848), marked B in fig. 3, appears only in the Starting Spectrum for the first 30 secs., and cannot be detected in any of the subsequent exposures.

With the object of discovering whether this phenomenon was peculiar to the mercury arc, similar experiments were made with a number of metallic arcs in air. Owing, however, to the unsteady running, during the essential early stages, nothing very conclusive was obtained except that in the case of the iron-arc an undoubted starting maximum was obtained for every condition of voltage and current employed.

\* Clark and Watters, Jour. Rönt. Soc. xvii. July 1922.



TABLE I.  
Energy Consumption and Radiation output of a mercury  
lamp. Low mains voltage 119 volts.

	Time.	Volts.	Amps.	Watts.	Tint %.
1 .....	0.15	22	3.2	70	133
2 .....	0.45	22	3.2	70	73
3 .....	1.15	23	3.15	70	33
4 .....	1.45	24	3.1	74	50
5 .....	2.15	28	2.95	82	60
6 .....	2.45	32	2.9	93	66
7 .....	3.15	35	2.75	96	66
8 .....	3.45	35	2.75	96	70
9 .....	4.15	35	2.75	95	70
10 .....	4.45	38	2.7	103	75
11 .....	5.15	41	2.6	107	80
12 .....	5.45	43	2.55	109	87
13 .....	6.15	44	2.45	108	90
14 .....	6.45	45	2.45	110	90
15 .....	7.15	45	2.5	112	90
16 .....	7.45	46	2.45	110	100
17 .....	8.15	47	2.4	110	100
18 .....	8.45	47	2.4	110	100
19 .....	9.15	47	2.4	110	100
20 .....	9.45	47	2.4	110	100
—	—	—	—	—	—
30 .....	15.15	48	2.3	110	100

TABLE II.  
Showing variation of output after striking the arc  
under different voltages.

Time.	Low Power. (Mains 119.)	Medium Power. (Mains 149.)	High Power. (Mains 160.)
0.15	133	100	45
0.45	73	40	25
1.15	33	40	40
1.45	50	45	45
2.15	60	47	45
2.45	66	50	47
3.15	66	60	50
3.45	70	75	60
4.15	70	75	70
4.45	75	75	75
5.15	80	75	75
5.45	87	80	75
6.15	90	80	75
6.45	90	80	85
7.15	90	90	90
7.45	100	100	100
8.15	100	100	100
8.45	100	100	100

Note that the tints are all expressed as percentages of the final steady condition for that experiment. With the higher mains voltage, the final output is greater and the tint therefore deeper than the corresponding tint obtained with a lower voltage. The final tints are in the ratio approximately 35 : 65 : 100.

LIV. *An Electrical Method for Tracing Stream Lines in the Two-Dimensional Motion of a Perfect Fluid.* By E. F. RELF, A.R.C.Sc., of the Aerodynamics Department, National Physical Laboratory\*.

IT has long been known that the equations giving (for two-dimensional systems) the stream lines in a non-viscous fluid and the equipotential lines in an electric field are identical. In both problems the equation

$$\nabla^2\psi = 0$$

must be solved subject to the condition that  $\psi$  has a constant value over every boundary, the actual values of  $\psi$  at the different boundaries depending upon the nature of the problem. The two-dimensional flow of a perfect fluid passing an obstacle such as an aerofoil can, therefore, be conveniently mapped if a suitable method can be found for tracing the system of equipotential lines due to a metal aerofoil placed in an electrostatic field. This field may be produced between two parallel metal plates, and the solution obtained is then equivalent to that of fluid flow past the obstacle and between parallel walls. The solution is practically unaffected when the dielectric between the plates is replaced by a substance of very low conductivity.

The apparatus described below was designed and constructed for use in the Aerodynamics Department of the National Physical Laboratory, in order that stream lines round an obstacle might be rapidly and accurately plotted in this way. A photograph of the apparatus is given in fig. 1. It consists of a concrete tank, 5 ft. long, 2 ft. 6 in. wide and 1 ft. 3 in. deep, filled with ordinary tap-water and coated inside with bitumastic enamel to prevent absorption of the water by the concrete. On the two longer sides are mounted thin sheets of aluminium, and the metal model of the obstacle to be studied stands in the centre of the tank.

The use of a steady potential difference between the two side plates leads to electrolytic troubles, and was abandoned in favour of an alternating potential difference of audible frequency, a telephone being used as an indicator. The resistance of the water between the plates is of the order of 100 ohms.

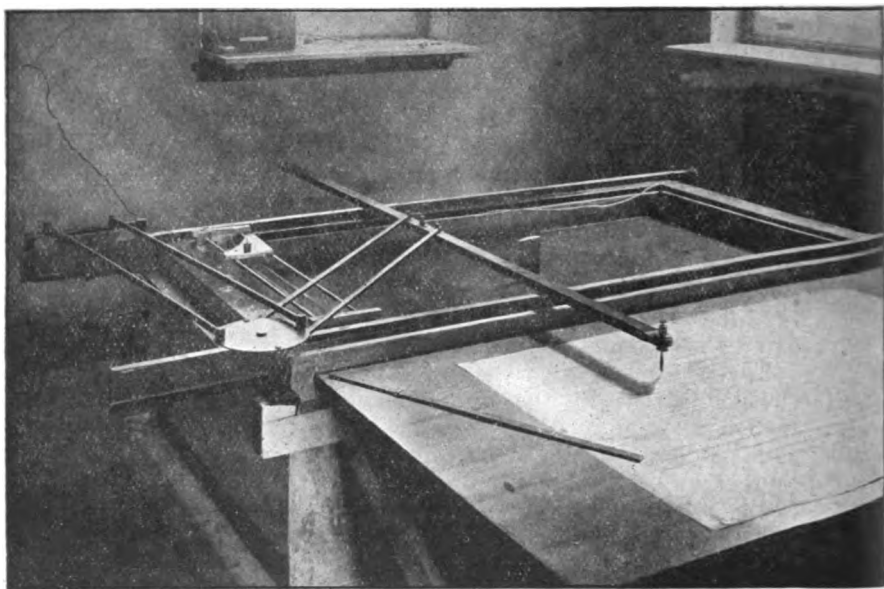
To determine the equipotential lines two exploring electrodes are used, consisting of fine platinum wires sealed into the ends of capillary tubes and projecting about 1/10 in. from the ends. One of these electrodes is fixed at any

\* Communicated by Mr. R. V. Southwell.

convenient point in the tank, while the other is carried on a pantograph of the drafting-machine type. This pantograph also carries a steel point, which copies exactly the motion of the exploring electrode over a drawing-board placed beside the tank.

The alternating potential difference is obtained from an oscillatory valve circuit in which the secondary and primary windings of an ordinary low-frequency inter-valve transformer are used in the plate and grid circuits respectively.

Fig. 1.

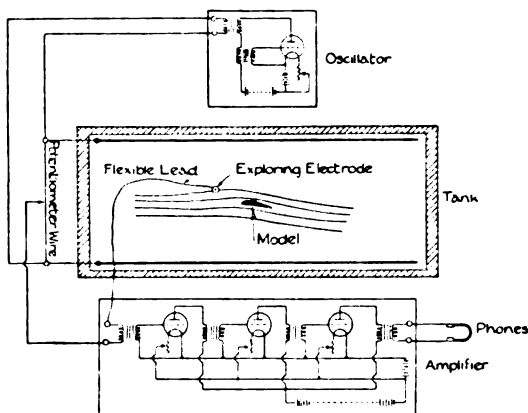


This circuit was found to oscillate at about 200 per sec frequency without the introduction of any capacity across the winding in the plate circuit, and gives a very constant and pure tone. The two exploring electrodes are connected to a three-valve low-frequency amplifier. A diagrammatic sketch of the apparatus, showing the electrical circuits, is given in fig. 2. The observer listens in the headphones connected to the output side of the amplifier, and adjusts the movable electrode until no sound is heard. The two electrodes are now at the same potential, and a mark is made by depressing the steel point on the pantograph so that it makes

a pin-prick in a sheet of paper fixed to the drawing-board. The process is repeated until sufficient points have been obtained to define the equipotential line passing through the fixed electrode. This electrode is then moved to a new position and another line drawn in the same way, and so on until the whole field is mapped. The process is very rapid in practice, and under good conditions the position of the movable electrode is determinable within about  $1/100$  in.

If it is desired to know the spacing between the equipotentials expressed as a fraction of the potential difference between the plates, a fine potentiometer wire is connected

Fig. 2.



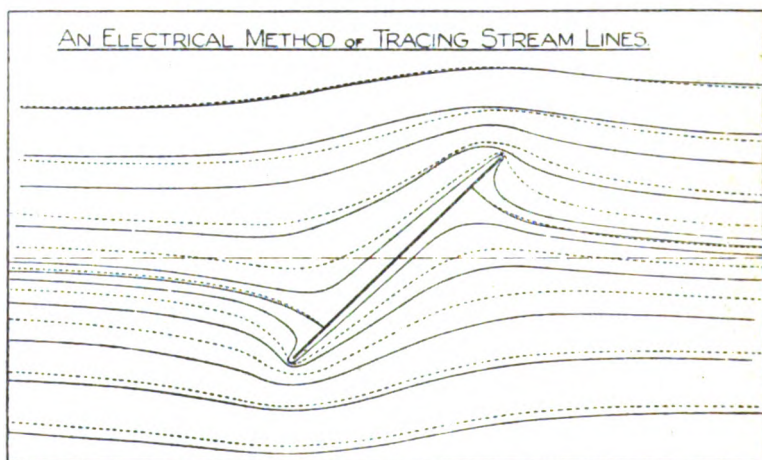
between the plates and points on this wire are employed to give reference potentials instead of the fixed electrode.

Used in the above way the apparatus will draw the stream lines of an inviscid fluid without circulation, because, since the model is insulated, the total electric flow across its boundary must be zero. The case in which circulation is present may be obtained by connecting the model to a point on the potentiometer wire, so that it is at a potential different from that which it would assume if insulated. In practice this method has not been used, on account of the difficulty of measuring the potential of the model, or the current flowing into it, in order to define the amount of circulation. Instead, the stream lines due to circulation alone are mapped by connecting both the side plates to one side of the alternating supply and the model to the other side, the potentiometer wire being used as before to supply the

reference potentials. The flow due to circulation of any desired magnitude can then be added graphically to that for non-circulatory flow.

Two illustrations of the results obtained with the above apparatus are appended, and problems were chosen for this purpose in which a direct comparison with theory was possible. The first of these (fig. 3) gives the stream lines for non-circulatory flow past a flat plate inclined at  $45^\circ$  to the direction of flow. The full lines were obtained by the electrical method, whilst the dotted lines were obtained from the hydro-dynamical equations. No attempt was made to measure the values of  $\psi$  for the various stream lines, and the comparison is accordingly to be made on the basis of the

Fig. 3.



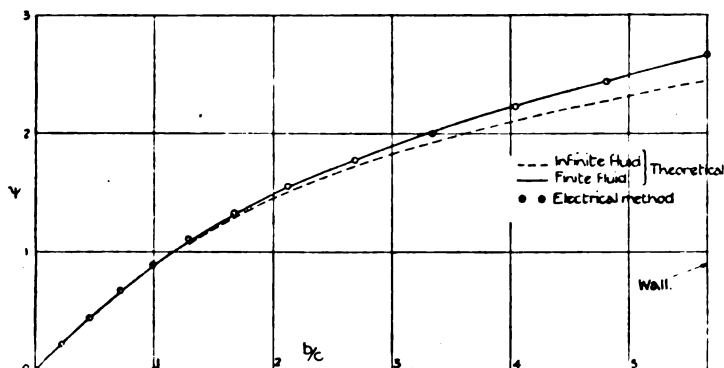
conformity of the two sets of stream lines. It will be noted that the two sets of lines agree remarkably well, even near the sharp edges of the plate, where the curvature is greatest.

The second illustration was obtained from measurements of the stream lines due to circulation only round the same flat plate. In this case the potentiometer wire was used as a reference, and it is possible to compare the actual values of  $\psi$ . This is done in fig. 4, which relates to the distribution of  $\psi$  along an axis bisecting the width of the plate at right angles. In an infinite fluid the stream lines for the flat plate are confocal ellipses with foci at the edges of the plate\*, and the dotted curve gives the values of  $\psi$  along the above line (*i. e.*, along the minor axes of the ellipses) for various values of  $b/c$ ,  $b$  being the distance from

\* Lamb, 'Hydrodynamics' (3rd edition), § 66.

the flat plate and  $2c$  the width of the plate. It was realized that the effect of the walls of the tank would not be negligible, excepting in the region very near the plate, and its effect upon the values of  $\psi$  along the chosen line was calculated by the method of images. This gave the full curve of figure 4. The points on the same diagram were obtained by direct measurement from the stream lines traced by the electrical method, the arbitrary scale of  $\psi$  (as given by the potentiometer wire) being so chosen as to make the potential at the side plates correspond with the calculated value of  $\psi$  (allowing for wall interference) at this distance from the plate. It will be seen that the agreement is very good indeed. It was noticed that although the presence of the

Fig. 4.



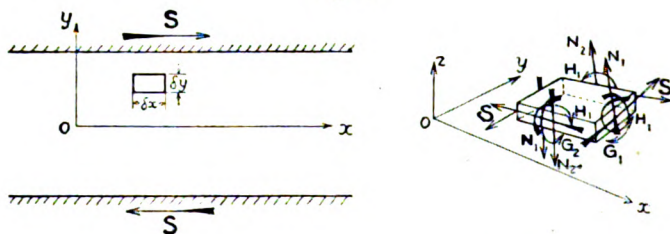
walls modifies considerably the values of  $\psi$  far from the plate, yet the stream lines, when plotted from the electrical determination, would be judged to be coincident with the system of ellipses given by theory for an infinite fluid. In other words, the change of shape of a given stream line which is produced by the introduction of the wall interference is not striking to the eye, although the actual value of  $\psi$  at a given point has been considerably altered. This fact serves to explain the agreement in the shape of the outer stream lines of fig. 3, where the comparison is with theoretical lines for an infinite fluid.

The apparatus is thus demonstrated to be sufficiently accurate for practical purposes, and it provides a very convenient and rapid method of solution of the stream-line problem in two-dimensional cases which can be conveniently represented in the electrical analogue.

LIV. *Note on the Stability of Laminar Shearing Motion in a Viscous Incompressible Fluid.* By R. V. SOUTHWELL, M.A., Superintendent of the Aerodynamics Department, National Physical Laboratory\*.

1. **I**N collaboration with Miss S. W. Skan†, I have recently investigated the effects of applied shearing forces upon the free transverse vibrations of a flat elastic strip. Fig. 1 shows the nature of the problem and the notation which was employed. To avoid unnecessary complication arising out of end effects, the length of the strip was taken as infinite and the transverse displacement assumed to be simply harmonic in  $x$ : under these conditions no restriction is imposed upon the wave-length of the displacement in a direction parallel to the edges, and the results were accordingly presented in diagrams which related the natural frequency of vibration with this wave-length and with the intensity of the applied shearing forces.

Fig. 1.



Two types of edge constraint were considered, namely, "simple support" and "clamping." The first type prevents displacement of the middle-surface at the edges, which are otherwise free; the second also prevents change of slope at the edges. The diagram corresponding to the second conditions is reproduced as fig. 2 of the present note: abscissæ are values of the ratio  $l/b$ , where  $l$  is the wave-length of the displacement and  $b$  the half-breadth of the strip; ordinates are values of  $b^2S/D$  (denoted by the symbol  $A$ ), where  $S$  is the intensity of the applied shearing forces per unit length of edge, and  $D$  is the "flexural rigidity" of the strip‡; and

\* Paper read at the International Congress for Applied Mechanics, Delft, 1924. Communicated by the Author.

† Roy. Soc. Proc. A, cv. pp. 582-607 (1924).

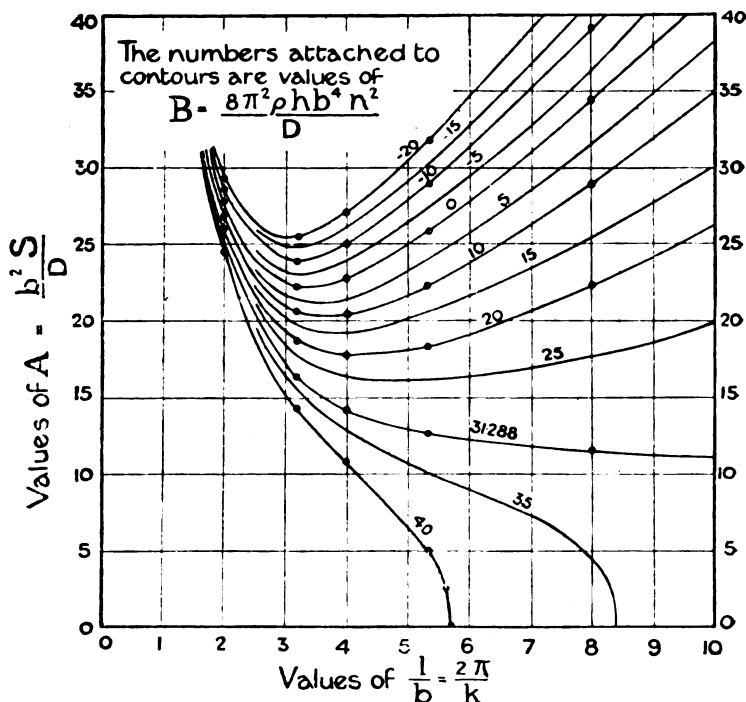
‡  $D = 2Eh^3/3(1 - \sigma^2)$ , where  $h$  is the half-thickness of the strip,  $E$  is Young's modulus, and  $\sigma$  is Poisson's ratio. Cf. § 2 of the paper cited.



the curves shown are contours drawn for constant values of the quantity  $8\pi^2\rho hb^4n^2/D$ , where  $n$  is the frequency of the transverse vibrations,  $\rho$  the density and  $h$  the half-thickness of the strip. Thus all the quantities which occur in fig. 2 are non-dimensional, and any consistent system of units may be employed.

It is evident from this diagram that an increase in the intensity of shear, for any definite value of the wave-length,

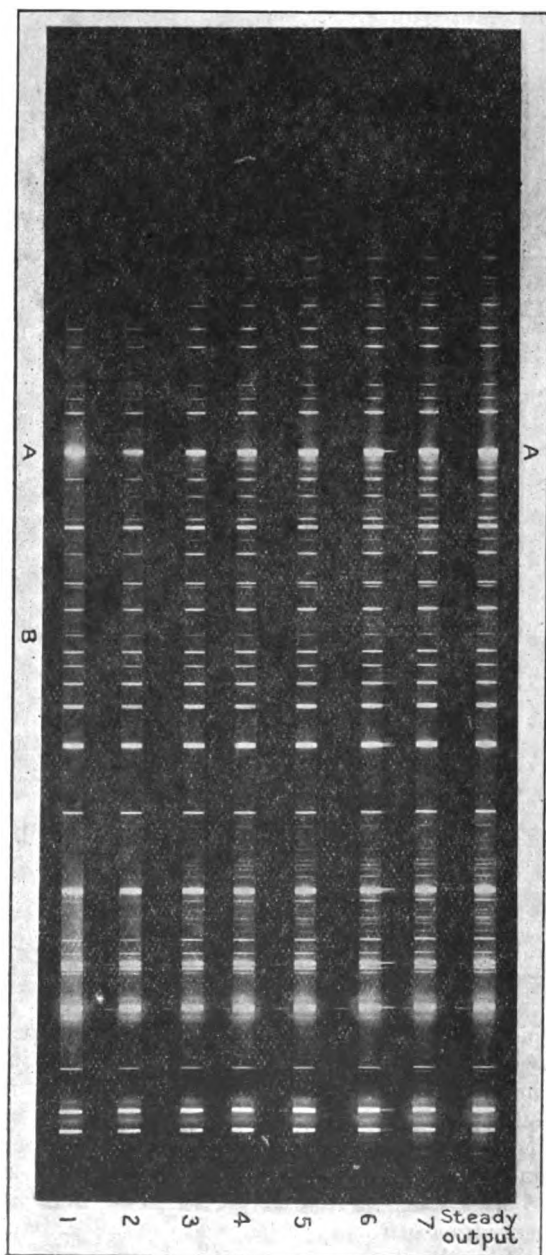
Fig. 2.



will be accompanied by a decrease in the value of  $n^2$ . At some particular value of  $S$  (corresponding to the contour numbered 0) the period of vibration becomes infinite and the distorted form can be maintained indefinitely, the elastic stability of the system being then neutral; whilst if  $S$  be increased beyond this value,  $n^2$  becomes negative, and the vibrations are characterized by an imaginary period,—i. e., the system becomes elastically unstable, and the transverse displacements increase (or decrease) exponentially in respect of time.



Fig. 3.



again. The most marked example is the line of wave-length ( $\lambda$  2536), which is marked A in the print. There can be little doubt that it is this line which is responsible for the effect under observation. It is interesting to note that in some earlier experiments this line was found to have by far the greatest photoelectric effect of all the lines of the mercury spectrum\*. The initial brilliance was somewhat exaggerated by the selectivity of the paper. It was found that this paper was sensitive throughout the whole range of the ultra-violet covered by the quartz spectrometer.

A print was made in the spectroscope directly on the paper by an exposure of over four hours, which showed that the yellow and green lines had little or no effect, whilst all the main lines in the ultra-violet were strongly marked. The selectivity of the printing paper thus accentuates any fluctuation in the ultra-violet region.

An attempt was made to record the fluctuations during periods of about 1 sec. A revolving shutter with a sector of  $180^\circ$  was used, but beyond confirming the fact that the intensity of  $\lambda$  2536 starts at a maximum value at the instant of striking the arc, nothing very conclusive could be obtained.

To measure any minor variation in intensity apparatus of precision would have been a necessity.

In order to summarise the evidence of the spectroscopic experiments, the lines may be divided into three groups. First, the lines which show a small but gradual increase of intensity as the lamp runs steady. Secondly, the lines which show an initial maximum followed by a drop and a steady rise. Thirdly, those which do not appear at all until an interval after the arc is struck. One minor line cannot be placed under any of these categories. This line ( $\lambda$  2848), marked B in fig. 3, appears only in the Starting Spectrum for the first 30 secs., and cannot be detected in any of the subsequent exposures.

With the object of discovering whether this phenomenon was peculiar to the mercury arc, similar experiments were made with a number of metallic arcs in air. Owing, however, to the unsteady running, during the essential early stages, nothing very conclusive was obtained except that in the case of the iron-arc an undoubted starting maximum was obtained for every condition of voltage and current employed.

\* Clark and Watters, Jour. Rönt. Soc. xvii. July 1922.

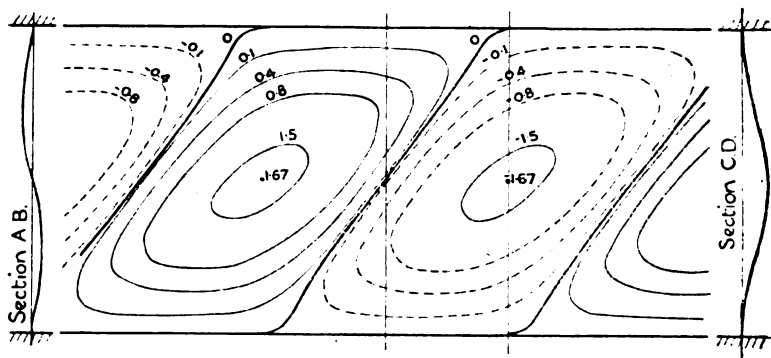
It is more natural to treat  $S$  or  $n$  as the specified quantity, since in reality, as was remarked above, no restriction is imposed upon the value of the wave-length. The diagram shows that in the absence of applied shear ( $A=0$ ) the gravest frequency of vibration corresponds to a displacement of two-dimensional type ( $l=\infty$ ), but that when  $S$  has a finite value the gravest frequency corresponds to a displacement having a finite wave-length; conversely, among vibrations having a specified frequency there is some one type, characterized by a finite wave-length, which requires a smaller shear than any other for its maintenance.

From a practical point of view, the most important conditions are those of neutral elastic stability, corresponding to the contour numbered 0 in fig. 2. Our calculations showed that the smallest shear required to produce these conditions, in a strip of which the edges are clamped, is given by

$$\frac{b^2 S}{D} = 22.18, \text{ approximately, } \dots (1)$$

and that the corresponding displacement has a wave-length about 1.6 times the breadth of the strip\*. It was thought

Fig. 3.



worth while to investigate the nature of the displacement in some detail, since experimental results could easily be obtained for comparison†, and a series of contours of constant displacement was accordingly plotted in a diagram which is reproduced as fig. 3 of the present note. The numbers attached to the contours have a relative significance

\* Cf. Table II. of the paper cited.

† A specimen strip, from a series tested in the Engineering Department of the National Physical Laboratory, was lent by Mr. H. Gough for reproduction (as part of fig. 1) in the paper cited.

only, the absolute magnitude of the displacement being indeterminate.

2. There is no direct connexion, either physical or mathematical, between the problem of elastic stability here treated and that of the stability of laminar shearing motion in a viscous fluid; but it is the purpose of the present note to show that results of the type given in equation (1) above have an application to the hydrodynamic problem. From (1), for example, we can at once deduce a result which has been previously obtained by W. M. Orr\*, whose formulation of the hydrodynamic problem has been accepted by Rayleigh† and H. Lamb‡, and will be followed here.

3. The equation which governs the vorticity of a viscous fluid moving in two dimensions is

$$\frac{\partial \zeta}{\partial t} + u \frac{\partial \zeta}{\partial x} + v \frac{\partial \zeta}{\partial y} = \nu \nabla^2 \zeta, \quad \dots \quad (2)$$

where  $\nu$  is the kinematic viscosity and  $\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2$ . The vorticity

$$\zeta = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y}, \quad \dots \quad (3)$$

where  $u$  and  $v$  are the component velocities of the fluid in the directions of  $x$  and  $y$  respectively.

In the case of uniform shearing motion between parallel planes  $y=0$  and  $y=d$ , the former of which is at rest, we have in the undisturbed motion

$$u = \beta y, \quad v = 0, \quad \zeta = -\beta, \quad \dots \quad (4)$$

where  $\beta$  is a constant. For the disturbed motion we may write

$$u = \beta y - \frac{\partial \psi}{\partial y}, \quad v = \frac{\partial \psi}{\partial x}, \quad \zeta = -\beta + \nabla^2 \psi, \quad \dots \quad (5)$$

where  $\psi$  is the stream-function of the disturbance. Then if the disturbance is infinitesimal (so that terms of the second order in  $\psi$  may be neglected) we have, on substituting from (5) in (2),

$$\left[ \frac{\partial}{\partial t} + \beta y \frac{\partial}{\partial x} - \nu \nabla^2 \right] \nabla^2 \psi = 0. \quad \dots \quad (6)$$

\* Proc. Roy. Irish Acad. xxvii. pp. 69-138 (1907).

† Phil. Mag. xxviii. pp. 609-619 (1914), or 'Collected Papers', vi. pp. 266-276. The notation employed in this note is substantially that of Rayleigh.

‡ 'Hydrodynamics', 3rd Ed. § 368.  $\zeta$  as defined by Lamb (and in the treatment here given) has twice its value as defined by Rayleigh, and is of opposite sign.

This equation must be satisfied by  $\psi$  at every point in the fluid field, whilst the condition of "no slipping at solid boundaries" requires that

$$\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial y} = 0, \text{ when } y = 0 \text{ and when } y = d. \quad (7)$$

In seeking to determine the conditions (if any exist) under which an accidental disturbance of the steady motion will tend to persist or to increase, we must ensure that such persistence is not in reality an effect of suitably varying pressure differences, implied in our solution, at the *ends* of the fluid field. This will be done if we make an assumption exactly similar to what was made for the elastic problem in § 1 above, and take the length of the fluid field to be infinite and the disturbance to be simply harmonic in  $x$ : our problem then becomes a limiting case of the problem of shearing motion between two concentric cylinders\*, in which the radii of the cylinders are infinite. We therefore suppose that  $u$ ,  $v$  and  $\zeta$ , in so far as they depend upon  $x$  and  $t$ , are proportional to  $e^{int} e^{ikx}$ , where  $n = p + iq$ ; and equations (6) and (7) then take the forms

$$\left[ \frac{\partial^2}{\partial y^2} - k^2 + \frac{q}{\nu} - \frac{i}{\nu} (p + k\beta y) \right] S = 0, \quad (8)$$

and where  $S = \nabla^2 \psi = \left[ \frac{\partial^2}{\partial y^2} - k^2 \right] \psi,$

$$\psi = \frac{\partial \psi}{\partial y} = 0, \text{ when } y = 0 \text{ and when } y = d. \quad (9)$$

The question of the stability of the steady shearing motion now turns on the sign of  $q$  in a disturbance of the type considered. If a solution of equations (8) and (9) can be found in which  $q$  has a zero or negative value, the steady motion will be neutral or unstable: if  $q$  is necessarily positive, the steady motion will be stable. The result due to Orr, of which mention has been made in § 2, is that no failure of the stability can occur unless the "Reynolds' number"  $\beta d^2/\nu$  exceeds 177, where  $d$  is the distance between the walls, so that  $\beta d$  represents their relative velocity. Whether failure

\* This problem has been investigated, both analytically and experimentally, by G. I. Taylor (Phil. Trans. Roy. Soc. A, ccxxiii, pp. 289-343, 1923), who has determined definite criteria of instability. The type of disturbance which is found to persist is, however, three-dimensional: it has no counterpart in the present problem.

can occur at some higher value of  $\beta d^2/\nu$  is a question which does not appear to have received a completely satisfactory answer, in spite of the skillful treatment which the problem has received from many workers\*: the general opinion seems to be that the steady shearing motion is completely stable for infinitesimal disturbances, but that the stability probably fails for finite disturbances, or (what is practically the same thing) when the walls are roughened by excrescences of finite size, if the Reynolds' number is sufficiently high.

4. To show that Orr's result can be obtained from the result for the elastic strip which has been stated in equation (1), we first consider the real form of the solution to (8) and (9) which corresponds to the symbolic form assumed in § 3. This may be written as

$$\psi = e^{-qt} \{ \Psi_1 \sin(kx + pt) + \Psi_2 \cos(kx + pt) \}, \quad (10)$$

where  $\Psi_1$  and  $\Psi_2$  are functions of  $y$  only, such that

$$\Psi_1 = \Psi_2 = \frac{d\Psi_1}{dy} = \frac{d\Psi_2}{dy} = 0, \quad \text{when } y=0 \text{ and when } y=d, \quad (11)$$

and

$$\left. \begin{aligned} [q + \nu \nabla_1^2] \nabla_1^2 \Psi_1 + (p + k\beta y) \nabla_1^2 \Psi_2 &= 0, \\ [q + \nu \nabla_1^2] \nabla_1^2 \Psi_2 - (p + k\beta y) \nabla_1^2 \Psi_1 &= 0, \end{aligned} \right\} \quad (12)$$

where  $\nabla_1^2 \equiv d^2/dy^2 - k^2$ , at all points in the fluid field.

It is easily verified by substitution that (10) is a solution of (6) and (7). If we now multiply the first of (12) by  $\Psi_1$  and the second by  $\Psi_2$ , add, and integrate between the limits  $y=0$  and  $y=d$ , we have, in virtue of the boundary conditions (11),

$$\begin{aligned} & \nu \int \{ \Psi_1''^2 + \Psi_2''^2 + 2k^2(\Psi_1'^2 + \Psi_2'^2) + k^4(\Psi_1^2 + \Psi_2^2) \} dy \\ & - q \int \{ \Psi_1'^2 + \Psi_2'^2 + k^2(\Psi_1^2 + \Psi_2^2) \} dy \\ & - k\beta \int (\Psi_1 \Psi_2' - \Psi_2 \Psi_1') dy = 0. \quad (13) \end{aligned}$$

Dashes here denote differentiation with respect to  $y$ .

5. We next consider the problem of a long flat strip in neutral elastic stability under the combined action (i) of a uniform shearing force, of intensity  $S$  per unit length, applied at its edges (exactly as in § 1) and (ii) of a uniform tension, of intensity  $T$  per unit length, acting in all directions in its plane. It can be shown† that the equation

\* References have been given by Rayleigh and Taylor in the papers cited.

† Cf. §§ 8 and 19 of the paper cited above. The axes and notation have been explained in § 1 of the present note.

which governs the transverse displacement  $w$  of points in the middle surface is

$$D\nabla^4 w - 2S \frac{\partial^2 w}{\partial x \partial y} - T\nabla^2 w = 0, \quad \dots \quad (14)$$

and hence the elastic stability of the system will be neutral if a solution of (14) exists which is simply harmonic in  $x$  (*cf.* § 1) and which satisfies the appropriate boundary conditions. When the edges are clamped, these are

$$w = \frac{\partial w}{\partial y} = 0, \text{ at the edges of the strip. } \dots \quad (15)$$

Suppose that a solution of this nature exists, and let it be represented by the expression

$$w = W_1 \sin kx - W_2 \cos kx, \quad \dots \quad (16)$$

where  $W_1$  and  $W_2$  are functions of  $y$  only, such that

$$W_1 = W_2 = \frac{dW_1}{dy} = \frac{dW_2}{dy} = 0, \text{ at the edges of the strip. } (17)$$

Then from (14) we have the equations

$$\left. \begin{aligned} [-T + D\nabla_1^2] \nabla_1^2 W_1 - 2kS \frac{dW_2}{dy} &= 0, \\ [-T + D\nabla_1^2] \nabla_1^2 W_2 + 2kS \frac{dW_1}{dy} &= 0, \end{aligned} \right\} \dots \quad (18)$$

and if we multiply the first of (18) by  $W_1$  and the second by  $W_2$ , add, and integrate over the breadth of the strip, we obtain, in virtue of the boundary conditions (17),

$$\begin{aligned} D \int \{ W_1''^2 + W_2''^2 + 2k^2(W_1'^2 + W_2'^2) + k^4(W_1^2 + W_2^2) \} dy \\ + T \int \{ W_1'^2 + W_2'^2 + k^2(W_1^2 + W_2^2) \} dy \\ - 2kS \int (W_1 W_2' - W_2 W_1') dy = 0. \quad \dots \quad (19) \end{aligned}$$

Dashes again denote differentiation with respect to  $y$ .

6. Equation (19) is the energy equation for the bent strip, expressing the condition that the work done by shear and tension, on the occurrence of the displacement  $w$ , is equal to the strain-energy stored by flexure. Now it has been shown

by Rayleigh\* that, in problems of the kind which we are considering, an approximate expression for the gravest natural frequency of vibration may be obtained directly from the energy equation, if we assume for the type of the displacement any reasonable form which satisfies the imposed boundary conditions; and further, that if the assumed type is not an exact solution of the differential equation of motion the result of the determination will err in the direction of *overestimating the stability of the system*. Thus in particular, if we use his method to determine the conditions of limiting elastic stability (zero frequency), we shall overestimate the magnitude of the disturbing forces required, unless the assumed displacement is an exact solution of the equation of neutral equilibrium.

Let us apply his method in this way to the elastic strip, and let us suppose further that the quantities which defined this problem in § 5 are related with those of the hydrodynamic problem of §§ 3 and 4 by the scheme

$$\left. \begin{aligned} D &= \nu, \\ -T &= q, \\ S &= \frac{1}{2}\beta, \\ 2b &= \text{breadth of elastic strip} \\ &= d. \end{aligned} \right\} \dots (20)$$

Then if, as our assumption in regard to the type of the displacement, we identify  $W_1$  and  $W_2$ , in (16), with the functions  $\Psi_1$  and  $\Psi_2$  of § 4, the relation (19) becomes identical with (13), and is therefore satisfied. But the equations (18) cannot be identified with (12), and hence our assumed type does not satisfy (14) exactly: it follows, by the theorem quoted above, that we shall overestimate the shear (or the thrust, if  $q$  is positive) required to bring about conditions of limiting elastic stability.

7. Now it was shown in the paper cited † that correct relations between shear, thrust (or tension) and flexural rigidity, under conditions of neutral elastic stability, can be obtained from the diagram reproduced in fig. 2 above. The necessary calculations have since been made ‡, and are described in the

\* 'Theory of Sound', i. §§ 88, etc.

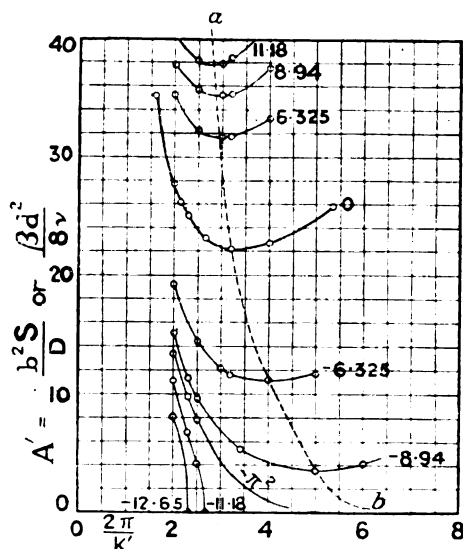
† *Loc. cit.*, § 19.

‡ I am indebted to Miss S. W. Skan for carrying out the laborious calculations involved in this part of the work.



Appendix to this note; the results are exhibited in fig. 4, where the coordinates are the same as in fig. 2, but the contours all relate to conditions of neutral stability ( $n=0$ ), under varying intensities of the tension  $T$ . The numbers attached to the contours are values of the non-dimensional quantity  $Tb^2/D$ : the particular values shown were chosen for convenience in calculation.

Fig. 4.



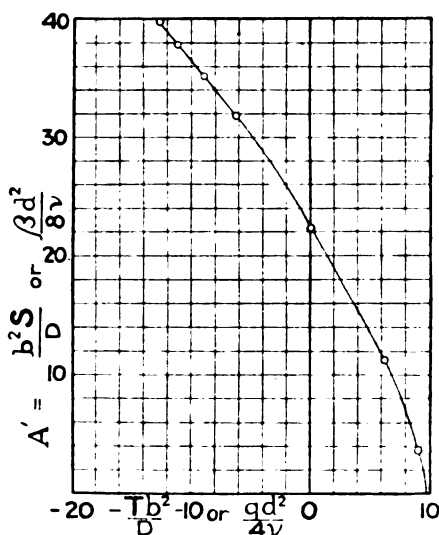
In fig. 4, the contour ( $Tb^2/D=0$ ) is identical with the contour numbered 0 in fig. 2. The contour numbered  $-\pi^2$  is asymptotic to the horizontal axis; the contour for any (algebraically) higher value of  $Tb^2/D$  exhibits a minimum corresponding to a displacement of some finite wavelength; and the contour for any lower value cuts the horizontal axis orthogonally\*. Thus for any contour value there is some lowest value of the ordinate  $b^2 S/D$ , given by the point of intersection of the contour with the dotted curve  $ab$  of fig. 4; and a curve may be drawn (fig. 5) to relate the applied tension  $T$  with the minimum value of

\* The complete diagram includes a part for negative values of the ordinate  $b^2 S/D$  which may be obtained by reflexion of fig. 4 with respect to its horizontal axis. Cf. § 16 of the paper cited.

the shear which must be superposed in order that conditions of limiting stability may result.

If the constants of the strip are specified by (20), fig. 5 may be interpreted as a relation between  $\beta$ ,  $q$ ,  $\nu$  and  $d$ ; and this relation, by the argument of § 6, will give a lower value of  $\beta$ , corresponding to any specified values of  $q$ ,  $\nu$  and  $d$ , than can occur in a solution of the hydrodynamic equations of § 3. We see that the value of  $\beta$ , when  $\nu$  and  $d$  are

Fig. 5



specified, increases steadily as  $q$  decreases, and in particular, that instability of the steady shearing motion ( $q$  zero or negative: *cf.* § 3) cannot possibly occur unless  $\beta$  exceeds a value given by

$$\frac{\beta d^2}{8\nu} = 22.18,$$

or

$$\frac{\beta d^2}{\nu} = 177, \text{ approximately.} \quad (21)$$

which is the value obtained by substituting from (20) in equation (1). This is Orr's result (*cf.* § 3).

Conversely, when  $\frac{\beta d^2}{\nu}$  has specified values, the curve of fig. 5 fixes lower limits for the value of the logarithmic

decrement  $q$  in the most persistent disturbance which can occur. These results are, so far as I am aware, new; but it should be emphasized that the fact of the curve extending to negative values of  $q$  does not necessarily imply that the steady shearing motion can become unstable for infinitesimal disturbances at any value of  $\beta d^2/\nu$ , however high.

## APPENDIX.

*Determination of Conditions of Neutral Elastic Stability for a Flat Strip subjected to Tension in combination with Shear.*

Methods for deriving these conditions from fig. 2 of the present note were indicated in § 19 of the paper cited. Relations were there given whereby any set of simultaneous values for shear, frequency and wave-length which constitutes a solution of the equations of vibration under shear alone can be transformed into a new set of simultaneous values of shear, tension, wave-length and frequency which also constitutes a solution.

When, as in the present instance, the new frequency is required to be zero, the relevant transformation equations\* are

$$\left. \begin{aligned} 2k'^2 + \frac{b^2 T}{D} &= 2k^2, \\ A'k' &= Ak, \\ k'^2 \left( k'^2 + \frac{b^2 T}{D} \right) &= k^4 - B, \end{aligned} \right\} \dots \dots (22)$$

where

$$\left. \begin{aligned} T &= \text{the tension per unit length, assumed} \\ &\quad \text{equal in all directions,} \\ l = \frac{2\pi b}{k} &= \text{wave-length of the transverse} \\ &\quad \text{displacement in a direction} \\ &\quad \text{parallel to the edges,} \\ A &= \frac{b^2 S}{D}, \\ B &= \frac{8\pi^2 \rho h b^4 n^2}{D}, \end{aligned} \right\} \dots \dots (23)$$

and where undashed values of  $k$  and  $A$  relate to the original solution, dashed values to the new solution.

From the first and third of (22) we have

$$B = \frac{1}{4} b^4 T^2 / D^2, \dots \dots (24)$$

\* numbered (39) in the paper cited.

showing that if a new diagram (fig. 4) is constructed in which contours of constant tension are plotted against

abscissæ representing  $\frac{2\pi}{k'}$  and ordinates representing  $A'$ ,

then any contour of constant  $B$  in fig. 2 will transform into a contour of constant tension in the new diagram. Given the contour value  $b^2T/D$ , and assuming a value for  $k'$ , we have  $B$  from (24) and  $k$  from the first of (22); then  $A$  may be found from fig. 2 and hence  $A'$  from the second of (22), so that a point on the required contour is determined.

Fig. 4 has been constructed from calculations, made on the foregoing lines, which are summarized in the table given below. For our present purpose we are mainly interested in the lowest values of  $A$  associated with any given value of  $b^2T/D$ : these minimum values correspond to points on the dotted line  $ab$  of fig. 4, and are related with  $Tb^2/D$  in fig. 5.

It may be remarked that the complete diagram, extending to negative values of  $A$ , would exhibit symmetry about the horizontal axis: this follows from the fact that fig. 2 possesses a similar symmetry\*. Hence, such contours in fig. 4 as intersect the horizontal axis will cut it orthogonally. The points of intersection are most easily found directly from the equation of neutral stability for a strip subjected to tension without shear; this is †

$$\left[ \frac{d^2}{dz^2} - k'^2 - \frac{b^2T}{D} \right] \left[ \frac{d^2}{dz^2} - k'^2 \right] Y = 0, \quad \dots (25)$$

and the boundary conditions require that ‡

$$Y = \frac{dY}{dz} = 0 \quad \text{when } z = \pm 1. \quad \dots (26)$$

To find the contour which is asymptotic to the horizontal axis of fig. 4 we make  $k'$  zero in (25). We thus arrive at the familiar solution

$$\left. \begin{array}{l} Y \propto (1 + \cos \pi z), \\ \frac{b^2T}{D} = -\pi^2. \end{array} \right\} \dots (27)$$

\* Cf. § 16 of the paper cited.

† Equation (13), modified in accordance with § 19, of the paper cited.

‡ Equations (15) of the paper cited.

TABLE.

$b^2T/D.$	B in fig. 2.	$k'$ (assumed).	$k$ from (22).	A from fig. 2.	$A' = Ak/k'.$	$2\pi/k'.$
12.65	40 .....	3.142	4.025	33.0	42.3	2.0
		2.513	3.558	28.3	40.0	2.5
		2.094	3.273	25.5 <sub>5</sub>	39.9	3.0
		1.967	3.192	24.8	40.2	3.2
		1.571	2.965	23.0	43.3	4.0
11.18	31.288 ...	3.142	3.930	32.2	40.3	2.0
		2.513	3.453	27.8	38.1	2.5
		2.094	3.159	25.2	37.9	3.0
		1.967	3.073	24.6	38.4	3.2
		1.571	2.839	22.9	41.4	4.0
8.94	20 .....	3.142	3.787	31.4	37.9	2.0
		2.513	3.287	27.3	35.7	2.5
		2.094	2.976	24.9	35.3	3.0
		1.967	2.890	24.1	35.4	3.2
		1.571	2.634	22.4	37.6	4.0
6.32 <sub>5</sub>	10 .....	3.142	3.610	30.7	35.3	2.0
		2.513	3.082	26.4	32.3	2.5
		2.094	2.748	24.2	31.7	3.0
		1.967	2.650	23.6	31.8	3.2
		1.571	2.373	22.0 <sub>5</sub>	33.3	4.0
-6.32 <sub>5</sub>	10 .....	3.142	2.590	23.3	19.2	2.0
		2.513	1.781	20.3	14.4	2.5
		2.094	1.106	23.0	12.1	3.0
		1.967	0.841	27.4	11.7	3.2
		1.571	0.834 <i>i</i>	-21.0 <i>i</i> *	11.2	4.0
		1.257	1.258 <i>i</i>	-11.7 <i>i</i> *	11.7 <sub>5</sub>	5.0
-8.94	20 .....	3.142	2.325	20.5	15.2	2.0
		2.731	1.729	18.0	11.4	2.3
		2.513	1.366	17.8 <sub>5</sub>	9.7	2.5
		1.837	1.047 <i>i</i>	-9.5 <i>i</i> *	5.4	3.42
		1.257	1.700 <i>i</i>	-2.7 <i>i</i> *	3.6	5.0
		1.047	1.837 <i>i</i>	-2.4 <i>i</i> *	4.2	6.0
- $\pi^2$	24.3 .....	3.142	2.222	19.3 <sub>5</sub>	13.7	2.0
		2.731	1.589	16.8	9.9	2.3
		2.513	1.183	16.7	7.9	2.5
		2.059	0.834 <i>i</i>	-9.7 <i>i</i> *	3.9	3.05
-11.18	31.288 ...	3.142	2.070	17.0	11.2	2.0
		2.731	1.367	13.5	6.8	2.3
		2.513	0.863	18.8 <sub>5</sub>	4.1	2.5
		2.364	0	0	0	2.66
-12.65	4.0 .....	3.142	1.833	13.8	8.3	2
		2.743	1.032	0	0	2.29

\* A calculated from equations (24) of the earlier paper cited.

More generally, we have

$$Y = P \sin \alpha z + Q \cos \alpha z + R \sinh k' z + S \cosh k' z, \quad (28).$$

where

$$\alpha^2 + k'^2 + \frac{b^2 T}{D} = 0, \quad . \quad . \quad . \quad (29).$$

and the criterion is

$$2(1 - \cos 2\alpha \cosh 2k') = \frac{\alpha^2 - k'^2}{\alpha k'} \sin 2\alpha \sinh 2k'. \quad (30)$$

Inserting any value of  $k'$  in (30), we can find  $\alpha$  by trial, and hence the value of  $\frac{b^2 T}{D}$  from (29).

#### LVI. *The Disappearance of Gas in the Electric Discharge (V.).*

*By The Research Staff of the General Electric Company, Limited, London\*.* (*Work conducted by N. R. CAMPBELL and E. G. NEW.*)

##### *Summary.*

THE purpose of these experiments is to discover a relation between the rate of absorption of a gas in the electric discharge and the rate of ionization of its molecules. It is pointed out that the true electrical absorption, dependent simply on ionization or allied processes, is entangled with other causes of absorption and evolution of gas; the main difficulty is to disentangle it.

The experiments show that, in nitrogen and carbon monoxide, the rate of absorption is proportional to the rate of ionization and, approximately at least, independent of the pressure, the speed of the ionizing electrons, and the arrangement of the electrodes. It depends very greatly on the condition, but not very greatly on the material, of the walls of the vessel. The number of molecules disappearing is often greater than the number ionized. In argon there is no evidence of an absorption simply related to ionization. In hydrogen the facts are obscure; but it is probable that there is an electrical absorption more rapid than in  $N_2$  or CO.

An attempt is made to explain the facts. In spite of the simple relation between absorption and ionization, it does not seem possible to hold that the ions are absorbed. Alternative theories are discussed: (1) that monatomic molecules liberated by ionization, (2) that partially ionized or excited molecules are absorbed; but both are open to grave objection. The molecules almost certainly are absorbed by reaction with the walls of the vessel, but no suggestion can be made as to the nature of the reaction.

\* Communicated by the Director.

Some observations, to be completed in a later paper, are described on the evolution of gas from glass vessels when heated, after they have been submitted to the usual processes of baking during exhaustion. It appears that there is no definite amount of gas that can be evolved by such heating, but rather that an equilibrium pressure is established.

The paper consists of the following parts:—

§ 1–2. Statement of the Problem.

§ 3–4. Experimental Methods.

§ 5. General Nature of the Results.

§ 6–11. Detailed Results. Effects of anode voltage (6); Arrangement of electrodes (7); Nature of gas (8); Pressure of gas (9); Nature of walls (10); Thermal evolution of gas (11).

§ 12. Comparison with Previous Work.

§ 13–17. Discussion of Results. Absorption and ionization (13, 14); Absorption and monatomic molecules (15); Absorption and excited molecules (16); Nature of absorption (17).

### STATEMENT OF THE PROBLEM.

1. **I**N the previous papers of this series\* we studied the disappearance of gas in the electric discharge, with special reference to the action of phosphorus. We put forward a theory to explain the specific effect upon the disappearance which phosphorus displays in common with certain other elements; and concluded that this effect was due to the formation of layers of chemically inactive phosphorus on the walls of the vessel; the gas appeared to adhere with particular avidity to such layers. But we did not offer any definite account of the circumstances which determine the adherence of the gas. If the disappearance is due to the electrical discharge, there should be some relation discoverable between the rate of disappearance on the one hand and, on the other, some quantities determining or determined by the discharge, such as the rate at which ions are formed, or at which they encounter the walls or other ions or neutral molecules, or the rate at which electrons strike the absorbing surface.

The experiments we are about to describe are concerned with this further problem. Since it appeared likely from

\* Research Staff of the G. E. C.: Phil. Mag. xl. p. 585 (1920); xli. p. 685 (1921); xlii. p. 227 (1921); xliii. p. 914 (1922).

our previous work, confirmed in this respect by our preliminary survey of the new field, that the presence of phosphorus and its congeners would be a disturbing factor, we have made no use of these elements: nothing was intentionally present in the vessels we used, except glass, metal, and the gas which was to disappear. A thermionic cathode was always used, and its presence will be assumed in the sequel.

Some guidance could be obtained from the work of others, which has been summarized by Dushman in his book 'High Vacuum' and in the articles collected therein\*. All writers find, as is to be expected, that the rate of disappearance of gas is proportional to the current carried by the discharge. Hughes† has compared the number of molecules disappearing with the number struck by electrons; he concludes that the ratio of these numbers is independent of the electron current, and that as many as one-sixth of the molecules struck may disappear. Dushman, Andrews, and Huthsteiner‡ have shown that at constant pressure and electron current the rate of disappearance is proportional to the pressure. All these experiments, which will be discussed later, indicate that the rate of disappearance is proportional to the rate of ionization; but little definite is known of the factor of proportionality.

2. However, though quantitative measurements are scanty, qualitative facts, which have been published by many writers and are familiar to all who attempt to obtain very high vacua, indicate clearly the lines along which experiments should be directed. The problem is obviously complicated, because the true electrical absorption that we are trying to investigate is partially masked by several other causes of the evolution or disappearance of gas. These we will mention and discuss briefly in turn, in order to explain the nature of our experiments.

(1). There is the chemical absorption investigated so carefully by Langmuir. It is chiefly noticeable with hydrogen in the presence of hot metals (especially tungsten), and with gases which undergo an "ordinary" chemical reaction with the material of the vessel. Other gases, such as  $N_2$  or CO, react with tungsten only when it is so hot that it has an appreciable vapour-pressure. This chemical absorption is easily distinguished from the electrical absorption,

\* S. Dushman, *General Electric Review* (1920, 1921).

† A. I. Hughes, *Phil. Mag.* xli. p. 778 (1921).

‡ S. Dushman, *General Electric Review*, xxiv. p. 671 (1921).



because it takes place in the absence of the field ; and it affects our experiments only in so far as it limits the choice of materials for investigation.

(2). There is an absorption of gas in or on new surfaces of the vessel, formed either by sputtering or by evaporation from some other part of it\*. Part at least of this absorption is independent of any electrical action, although (as in the case of phosphorus) it may influence electrical absorption greatly. In such experiments as ours it must be avoided by using low potentials and comparatively low temperatures of the thermionic cathode, and thus reducing sputtering and evaporation.

(3). On the other hand, there is an evolution of gas which appears purely thermal and depends on the present state and past history of the vessel as regards temperature, and on the gas that has already disappeared in it. It is an obscure matter which we are still investigating and on which we hope to publish more later. We have only once (and that under unknown conditions) obtained a vessel in which the pressure did not increase regularly as the temperature was raised ; and we have never obtained one in which the pressure would not increase slightly on standing at constant temperature after gas had disappeared in it. But this evolution can be reduced to a minimum by prolonged baking of the vessel at the highest permissible temperature and in the best possible vacuum before experiments begin ; such precautions were always taken ; the effect on our results of the residual evolution, which could not be eliminated, will be discussed later.

(4). There is an electrical evolution of gas independent of the thermal evolution, part at least of which has been traced to the impact of electrons upon surfaces charged with gas. There is evidence that the electron stream can drive off gas from the anode, even if it produces no appreciable rise in general temperature (see further, p. 562). It is perhaps to be expected that a similar evolution of gas should be produced by a stream of positive ions ; for such evolution would be no more than an aspect of cathodic sputtering. As will appear later, it is much more difficult to produce direct evidence of such evolution or to disentangle it from the electrical absorption ; but the available evidence indicates that it is not a material factor in our experiments.

\* See S. Dushman, *General Electric Review*, xxiv, p. 439 *et seq.* (1921).

EXPERIMENTAL METHODS.

3. The vessels in which the disappearance of gas was studied were usually triodes. The cathode was usually a tungsten filament, but a few observations were made with oxide-coated filaments made of platinum or platinum alloy by the Western Electric Company\*. It was surrounded by a nickel-wire spiral, similar to the grid of a receiving valve; indeed, the parts used were actually derived from R-5-volt valves of the M.O. Valve Company. The third electrode was either a nickel cylinder surrounding the spiral, similar to the anode of such a valve, or a layer of silver covering partially or almost completely the surface of the glass bulb. The volume of the bulb was usually 150 c.c., but bulbs of 80 and 350 c.c. were also used; they were sometimes connected by side tubes to other vessels, and the total volume of gas of the apparatus thereby increased. Most of the experiments were made with 150 c.c. bulbs with the cylinder surrounding the spiral (Type A), or similar bulbs with the surface almost completely silvered (Type B). In one vessel of type B the silvered surface was replaced by a nickel gauze fitting closely to the glass. The absorption in this vessel was indistinguishable from that in those with the silvered surface.

The electrical circuit of the triode was that appropriate to its use as an ionization manometer. But it was found in the preliminary experiments that much more consistent results were obtained if, by a reversal of the usual practice in valves, the electrode of smaller area (the spiral) was made positive to the filament and the electrode of the larger area (the cylinder or the silvered wall) negative to the filament. The reason is to be found in the electrical evolution, already mentioned, arising from the impact of electrons on gas containing surfaces; the smaller the area on which they impinge, the smaller the evolution. This arrangement was adopted unless the contrary is stated. In order to avoid confusion, the negative electrode, receiving the positive ions, will be termed the "collector" and not the "grid"; the latter term suggests the electrode of small area, whereas the collector was usually the electrode of larger area.

$V_a$ , the voltage between cathode and anode, ranged from 50 to 350 volts;  $V_g$ , the voltage between cathode and collector, was usually 2 volts; but the value of  $V_g$ , so long

\* To whom we would express our thanks for their courtesy in supplying us with some of their wire.

as it was of the right sign, was quite without effect on the experiments.

The gas used in most of the experiments, and that assumed when no contrary statement is made, was nitrogen nearly free from argon. Other gases will be discussed later (§ 8). It was introduced through the liquid-air trap after baking and exhaustion of the vessel and just before it was sealed off from the pump. The initial pressure was usually about 0.001 mm.

#### *The Measurements.*

4. Measurements were made of the electron current flowing to the anode  $i_a$  ( $10^{-6}$  to  $10^{-4}$  amp.), the positive-ion current flowing to the collector  $i_g$  ( $10^{-8}$  to  $2 \times 10^{-7}$  amp.) and the time  $t$ . The pressure is measured by  $i_g/i_a$ . If we write

$$p = \alpha \frac{i_g}{i_a}, \quad . . . . . (1)$$

$\alpha$  was independent of  $p$ ,  $i_a$ ,  $V_g$  within relevant limits of accuracy for most of the vessels. The mean free path of the electrons, calculated from  $\alpha$ , was always greater than the largest dimension of the bulb, because the electrons oscillated to and fro before finally falling into the small anode; it also increased with  $V_a$ .  $\alpha$  was determined for each vessel, each  $V_a$ , and, if necessary, for each pressure, by a calibration, direct or indirect, in terms of a McLeod\*.

The results are best expressed in terms of the ratio between  $n_1$ , the number of molecules disappearing per unit time, and  $n_2$ , the number of ions formed in the same time. If there is no recombination, and the ions are all singly charged, while

$$n_2 = i_g/\epsilon, \quad . . . . . (3)$$

$$n_1 = -NV \frac{dp}{dt}, \quad . . . . . (3)$$

where  $N$  is the number of molecules in unit volume of the gas at unit pressure and room temperature,  $V$  the volume of the vessel, and  $\epsilon$  the charge on an electron.

Consequently

$$\frac{n_1}{n_2} = -\alpha VN \epsilon \frac{1}{i_g} \frac{d}{dt} \left( \frac{i_g}{i_a} \right), \quad . . . . . (4)$$

\* A recent letter ('Nature,' 112, p. 651 (1923) has been interpreted as challenging the reliability of the McLeod. Of course it is perfectly reliable if care is taken to avoid the presence of vapours; but the precautions necessary for this purpose are not always realized.

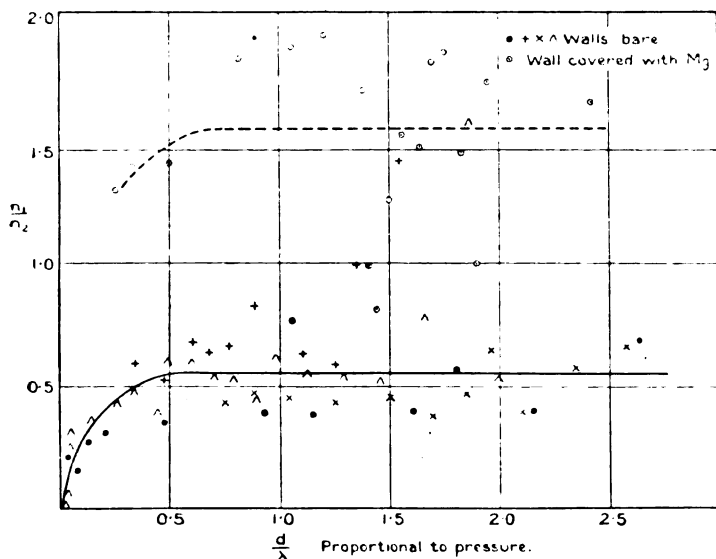
and all the quantities on the right-hand side can be measured. Again, in the expression of the results, it is best to replace the pressure by the ratio  $d/\lambda$ , where  $d$  is some length characteristic of the vessel and  $\lambda$  is the mean free path of one of the particles concerned; this ratio is, of course, proportional to the pressure. Actually  $d$  has been taken to be the greatest distance between anode and collector,  $\lambda$  the free path of the neutral molecule;  $d/\lambda$  will therefore be some measure of the number of collisions a positive ion is likely to make during its passage through the vessel.

No great precision was attempted in any of the measurements; for it was clear that sources of variation were present which would mask completely any mere experimental errors. But the absolute errors do not exceed 10 per cent.

#### GENERAL STATEMENT OF RESULTS.

5. Fig. 1 shows the main features of the results obtained in a vessel of type A,  $n_1/n_2$  being plotted against  $d/\lambda$ .

Fig. 1.



Typical Absorption Curve.

Curves of this nature will hereafter be termed "absorption curves." The points other than the circles show the results of four independent experiments, between which the vessel was opened, re-pumped, and re-filled with gas. These four

experiments agree with each other about as well as any similar set that has been made. They define quite certainly the general form of the curve represented by the solid line ; but the departure of individual points from that line is so great that a larger number of observations is necessary to arrive at any quantitative conclusions. Each of the four experiments shown requires about 8 hours' continuous observing ; it will be realized, therefore, that the experiments are exceedingly laborious, and that it is not a simple matter to secure measurements which will answer all the questions which may be raised.

There are three features of the curve to which attention should be directed :—(1) At the higher pressures,  $n_1/n_2$  is nearly independent of the pressure ; but (2) at lower pressures it decreases rapidly with the pressure, and tends to zero. (3) The constant maximum value of  $n_1/n_2$  is not much less than 1. These three features are characteristic of all the observations that have been made with nitrogen. In some cases the distribution of the experimental points is so irregular that it would have been impossible to decide from these points alone even the general shape of the curve ; but the constancy of the form, whenever it was definite, together with the absence of any evidence in favour of any other form, appears to us conclusive. The only doubt that we have is whether the straight part of the curve is really horizontal ; there was sometimes an indication of a small constant increase of  $n_1/n_2$  with the pressure.

The circles illustrate other important features characteristic of all our experiments. These measurements were made on the same vessel as the remainder ; but just before filling the vessel with gas, the collector cylinder was heated by electron bombardment, and a small quantity of magnesium metal attached to it was thereby evaporated and deposited on the glass walls of the bulb ; the metal film so formed was insulated during the observations and had no appreciable influence on the nature of the discharge. In this experiment the results of this process were two. In the first place the points become very irregular ; indeed, they are as irregular as in any experiment we have made not open to suspicion ; they are given for that reason. The dotted line is drawn of the form shown, only because, as has been said, the general evidence indicates that this form is universal. But this is purely accidental. We have never been able to decide why some experiments are so much more irregular than others, and there is no evidence that such deposition of a metal on the walls tends either to produce or to remove

irregularity. In the second place the values of  $n_1/n_2$  are increased, and are now in general greater than 1. This is not accidental. We have always found that the value of  $n_1/n_2$  is largely determined by the treatment of the walls of the vessel, and that it is increased by any change (such as very prolonged baking or the deposition of a new film) which is likely to produce a surface relatively free from adherent gas. Further, we always find that, when such a surface is produced, the constant maximum value of  $n_1/n_2$  is greater than 1.

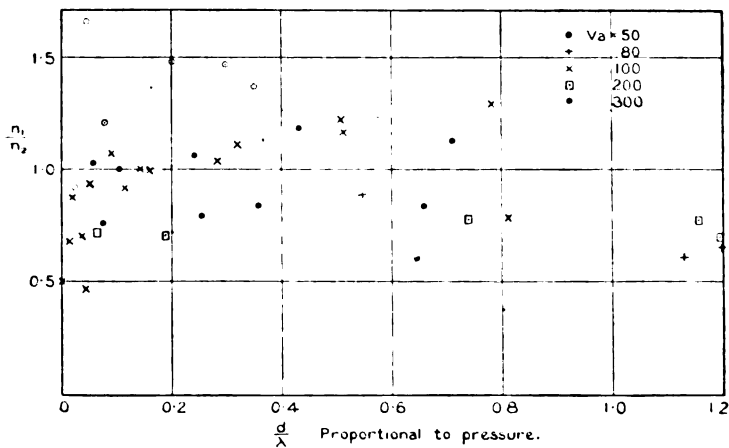
After this preliminary survey to indicate the points to be investigated, we will proceed to a more detailed account of the facts. Experiments have been directed chiefly to the influence upon  $n_1/n_2$  of (1) the nature of the discharge, (2) the nature and quantity of the gas, (3) the nature of the walls.

### DETAILED RESULTS.

#### Anode Voltage.

6. Our first question is whether  $n_1/n_2$  is independent of the means by which the ionization is produced. Is it independent of  $V_a$ , which determines the speed of the ionizing electrons, and of the arrangement of the electrodes?

Fig. 2.



Variation of  $\frac{n_1}{n_2}$  with  $V_a$  (Vessel B).

The effect of  $V_a$  was investigated by repeated experiments in the same vessel, in each experiment a pair of values of  $V_a$  being compared. Fig. 2 shows the results, the different

kinds of points referring to different voltages. It is clear that  $n_1/n_2$  is greater with  $V_a=50$  than with higher values. But these points are unreliable; for with such a low value of  $V_a$ , a study of the relation (1) showed that the positive-ion current was not saturated, and that all the positive ions were not arriving at the collector; some were disappearing by recombination.  $n_2$  is consequently greater than  $i_p/\epsilon$ , and the values of  $n_1/n_2$  calculated from (4) are too high. For the remaining values of  $V_a$ , from 80 to 300 volts, there is no evidence of a dependence of  $n_1/n_2$  on  $V_a$ ; the points seem to lie on two distinct curves, but each curve includes points with high and low values of  $V_a$ . It may be concluded, therefore, that the speed of the ionizing electrons within these limits has no very great effect on the rate of absorption, so long as the number of ions formed is the same.

This result has a subsidiary importance. If, as suggested on p. 556, there were an electric evolution, of the nature of sputtering, due to the impact of the positive ions on the collector, it should increase rapidly with  $V_a$ , and consequently the apparent value of  $n_1/n_2$  decrease with  $V_a$ . Since no rapid variation is found, it may be concluded that if there is an appreciable evolution of this kind, it is not similar to sputtering.

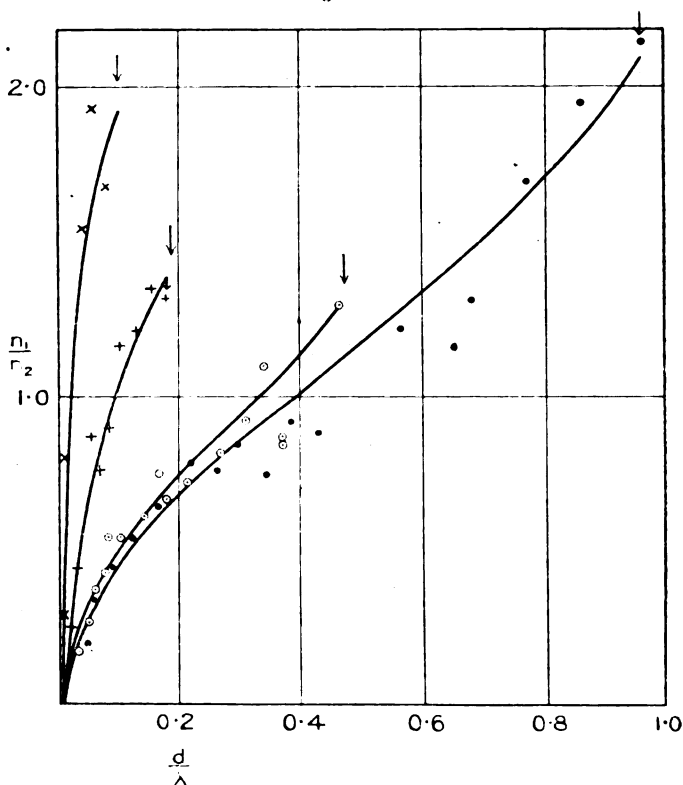
#### *Area of Electrodes.*

7. Another method of varying the nature of the discharge is by changing the disposition of the electrodes. In the earlier experiments the electrodes were connected as in a valve, the larger electrode being the anode. Fig. 3 shows the results of some experiments with this arrangement in a vessel of type B, the wall, silvered almost completely, being the anode. The curves are totally different from those of fig. 1;  $n_1/n_2$  increases continuously with the pressure. Moreover, the disposition of the curve varies with the initial pressure (indicated by the arrow);  $n_1/n_2$  initially is approximately the same whatever the initial pressure; but the higher the initial pressure, the less is the value of  $n_1/n_2$  at any lower pressure.

The reason for this difference has already been suggested; it appears at once if experiments are made alternately with the large electrode as collector and as anode. If it is first made the collector, and some portion of the gas is absorbed, and if it is then made the anode, the immediate result of the discharge is an increase in pressure; after a time the increase ceases and is replaced by a decrease, which gives a value not very different from that obtained in the previous

observations with the large electrode as the collector. If the connexions are reversed once more and the large electrode made collector, there is no appreciable increase, but absorption begins immediately with a value of  $n_1/n_2$  not very different from that obtained originally.

Fig. 3.



Absorption Curves with Large Electrode as Anode.

It seems clear, therefore, that the impact of electrons upon the large electrode can liberate from it gas which has been absorbed by the discharge (and probably gas adherent to it from any other reason); the electronic current liberates gas from the large electrode, and not (to the same extent at least) from the small, simply because there is more gas adhering to the large electrode. The continual decrease of  $n_1/n_2$  when the discharge is run continually with the large electrode as anode, is due to the continual increase in the



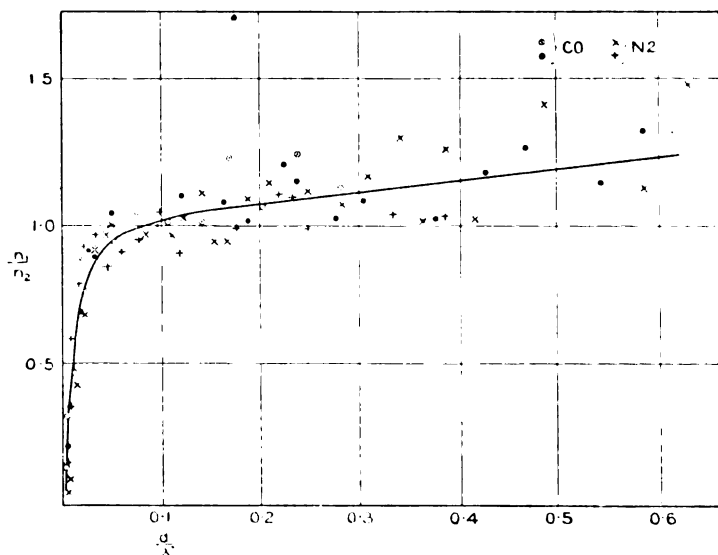
amount of gas absorbed on it and, consequently, in the rate of evolution counteracting the absorption.

There seems no doubt that this explanation is correct in outline; and, if that be so, experiments with the large electrode as anode are not likely to lead directly to a solution of our main problem. But there is one curious feature which suggests that there are further complications. In the experiments when the two arrangements of the electrodes are used alternately, the greatest value of  $n_1/n_2$  when the large electrode is the anode is consistently greater than the greatest value when it is the collector; it may be nearly twice as great. To this matter we shall return in the discussion.

#### *Various Gases.*

8. The only other gas in which results closely similar to those for nitrogen were obtained is carbon monoxide, which

Fig. 4.



Absorption of CO and  $N_2$ .

was introduced into the vessel by bombarding a nickel anode in an attached vessel. Fig. 4 shows the results of successive experiments in the same vessel with this gas and with nitrogen. There is no certain difference between the two gases. An attempt at a closer comparison was made by

introducing the two gases into the same vessel without opening it and repumping, the nitrogen in this case being liberated by breaking a bulb; the attempt was unsuccessful for a reason to be mentioned later.

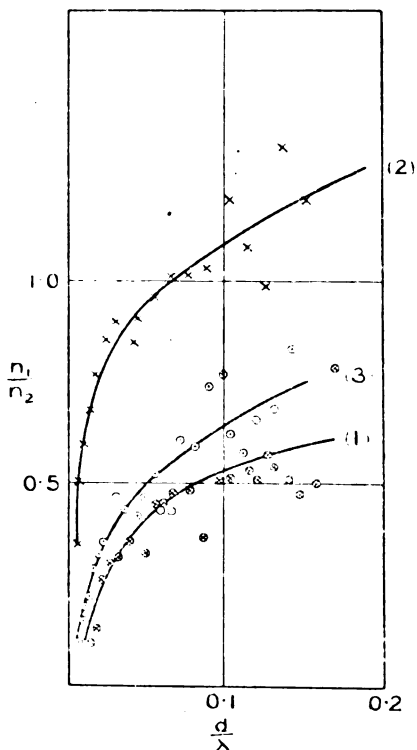
Measurements were made in argon. Here no definite absorption could be obtained of the same order as that in nitrogen;  $n_1/n_2$  was always less than 0.1. This result is contrary to that of Dushman, Huthsteiner, and Andrews (*loc. cit.*), who found that argon was absorbed at half the rate of nitrogen. But it is not clear that sputtering was avoided in their experiments. Argon and other inactive gases can certainly be made to disappear if considerable sputtering is in progress; but we have not been able to satisfy ourselves that it will disappear, like nitrogen, in virtue of ionization and in the absence of appreciable sputtering.

Attempts were also made to investigate hydrogen and oxygen. With these gases a tungsten cathode cannot be used; it was replaced by an oxide-coated cathode. Experiments with nitrogen showed that in this gas the measurements were quite independent of the nature of the cathode, a very complete comparison being obtained in a vessel provided with a tungsten cathode at one end and an oxide cathode at the other. No trace was found of the abnormal clean-up described by Hughes (*loc. cit.*). In oxygen there was complete failure, for the pressure of the gas changed when the cathode was heated in the absence of any field. The changes were complex, and were not always in the same direction. The matter has not been investigated further, for the changes were so large compared with any practicable rate of absorption due to ionization that it was clearly impossible to attain the main object of the experiment. In hydrogen there is also a change of pressure due to the mere heating of the cathode; as Hughes has found (*loc. cit.*), the pressure decreases, as it does in the presence of hot tungsten, but much more slowly. It was possible, therefore, to obtain conditions in which the disappearance of gas proceeded far more rapidly when the gas was being ionized by the application of the anode voltage than when it was not. If it is assumed that the two processes of absorption are independent, then the experiments showed that  $n_1/n_2$  for hydrogen was considerably greater than for nitrogen; it was about twice as great. But the observations were not very regular, and the assumption on which their interpretation is based is by no means certain. The general form of the absorption curve is

probably not quite the same as in nitrogen, the straight part of the curve being inclined upwards, as in fig. 5 below.

Before any of these pure gases had been tried, a great number of preliminary experiments had been made with "residual gas" either left in the vessel by stopping the pump for a suitable period before sealing off or liberated

Fig. 5.



Residual Gas in Large and Small Vessels.

(1) and (3), Small Vessels.

(2), Large Vessels.

after sealing off by baking (see p. 571). The experiments were less regular than in nitrogen, but in the best series of experiments, shown in fig. 5, some consistency was obtained; the significance of the different curves in this diagram will be stated later. Here it seems clear that the straight part of the curve is not horizontal, but that there is a continual increase of  $n_1/n_2$  up to the highest pressures observed.

However, owing to great irregularities in the earlier experiments, the curves were not carried so far as those taken later.

The question of course arises what is the nature of this "residual gas." Attempts were made to identify it by determining its ionization and resonance potentials, and comparing them with that of known gases in the same vessel. The method is not very accurate at pressures of a few thousandths of a millimetre; but the results indicated strongly that the gas is carbon monoxide. However, the difference in the shape of the curves of figs. 4 and 5, which seems real, suggests that it is not pure carbon monoxide, though no critical potentials which could be associated with another gas could be found. Hydrogen is the most probable admixture. On the other hand, if hydrogen is present it should disappear in the presence of hot tungsten without ionization by a field; but no change of pressure could be detected unless the field was applied. It is possible that carbon monoxide favours the action of the walls in catalyzing the reverse reaction, converting atomic into molecular hydrogen\*; but the matter cannot be cleared up for the present.

#### *Effect of Pressure of Gas.*

9. Another question which arises concerns the effect of the pressure of the gas present. It is answered partially by the form of the absorption curves already given, which show that there is a considerable range of pressure, at least in nitrogen and carbon monoxide, within which  $n_1/n_2$  does not vary rapidly with the pressure. But there is a possibility that, when the pressure is so high that the free path of the ions is small compared with the distance between the electrodes, the relation changes its form; such a change is almost inevitable at some stage if, at the lower pressures, there is a steady increase of  $n_1/n_2$  with pressure. The vessels used in these experiments were not suitable for measurements at pressures much higher than those shown; indeed, as we found in previous work†, it is always difficult at higher pressures to measure the number of positive ions formed; we cannot, therefore, answer this question definitely. But it is important, in order that our present work may be connected with that described in our earlier papers. In those papers the initial pressure was of

\* See R. W. Wood, *Phil. Mag.* xliv. p. 538 (1922).

† *Phil. Mag.* xlii. p. 227 (1921).

the order of 0.1 mm., whereas now it is of the order of 0.001 mm. Is the process the same in the two cases? In reply, we can only point out that there appears to be perfect continuity between the two processes, and that such estimates as can be made, necessarily very rough, of  $n_1/n_2$  at the higher pressures, indicate values certainly not much lower and possibly a good deal higher than those obtained at the lower. We believe that the two processes are essentially the same, but that complicating factors, to be discussed later, enter at the higher pressure.

### *Effect of the Walls.*

10. Our observations in this matter may be summarized in the statement that the material of the wall is relatively unimportant, but (as might be expected) any treatment of the walls which tends to rid them of adherent gas or to prevent the evolution of that gas, produces at the same time an increase in the true rate of absorption (and not merely in the apparent rate).

Thus, prolongation of the baking and pumping in a very high vacuum increases the absorption, though a limit appears to be reached after which no improvement is possible. Bombardment of the electrodes by electrons has the same effect, quite independently of a liberation of gas from the body of the metal in virtue of increased temperature. Cooling the wall of the vessel in liquid air during the discharge again increases absorption, and all the gas absorbed is not liberated when the liquid air is removed. Lastly, the deposition of a film of any material on the walls while the vessel is evacuated increases absorption.

In this last observation we are clearly repeating the results that we described at length in our previous paper\*, which was concerned with much higher pressures. Again, we have been unable to establish any connexion between the nature of the film deposited and the absorption: but the results are so capricious that we are not prepared to assert that there is no connexion. The materials we have tried are tungsten, magnesium, copper, silver, cryolite, glass, and phosphorus. In the case of phosphorus the effects are complicated by the action of the discharge on the deposited film, which is discussed at length in our earlier papers (*loc. cit.*). On the other hand, the conditions of deposition have a marked effect, especially the pressure obtaining in the vessel when the deposition occurs. If the pressure is too

\* Phil. Mag. xliii. p. 914 (1922).

high before the evaporation is started, or if a considerable quantity of gas is liberated at the same time as the vapour of the substance to be deposited, then there is a marked decrease in absorption. If gas is present during the evaporation, some of it is always absorbed during the process, as Langmuir has proved in the case of tungsten; and in some cases there appears to be a slow absorption without the discharge after the new film is deposited. Care was, of course, taken that the experiments on absorption by means of the discharge were not started until the pressure in the absence of the discharge was constant; the increased absorption observed cannot be simply due to an effect independent of the discharge. But it may be asked whether the similarity found between all newly deposited films was not due to their being all actually covered with the same layer of absorbed gas. We are clear that they cannot have been completely covered, because in some cases the total quantity of gas which had access to the film between the evaporation and the starting of the absorption experiment was much less than that required to form a monomolecular layer over the whole surface.

The area of the walls appears also to affect the absorption, which is larger in the larger vessel. This point is illustrated in fig. 5, where the upper curve refers to a bulb of 350 c.c. volume, the lower pair to one of 70 c.c. volume. The two bulbs were in connexion, they contained the same electrodes, and the values of  $\alpha$  were nearly the same. (When the spiral is used as anode,  $\alpha$  does not depend greatly on the volume of the vessel.) The curves were taken in the order 1, 2, 3, gas being liberated after each experiment by baking the vessel. There is no doubt of the effect of volume, but the ratio between the absorptions is not so great as the ratio of the areas of the vessel.

The "fatigue" of the absorption was also investigated. For this purpose the absorption vessel was connected to another in which carbon monoxide could be liberated by the heating of a nickel anode. Successive portions of gas were thus introduced and absorbed. A progressive decrease in the rate of absorption was produced, each absorption curve being generally lower and beginning to fall away markedly at a higher pressure. The decrease of absorption became perceptible when a quantity of gas had been absorbed which would cover a tenth of the walls with a monomolecular layer; the absorption became too slow to observe accurately, having fallen to about one-tenth of its original value, when a quarter of a monomolecular layer had been absorbed. It

was this fatigue which prevented the comparison of different gases by successive absorption in the same vessel (see p. 565).

Here it may be recorded that the greatest value of  $n_1/n_2$  we have ever actually observed in a single observation is 13. and the greatest value constant over a considerable range of pressure 10.5. But there are doubts about these values. They were obtained in a vessel in which the collector was a squirrel-cage lamp filament, the anode being the usual spiral. The total area of the electrodes was therefore very small. In such conditions there is much doubt whether  $i_g$  measures the number of positive ions. There was a certain range of pressure over which  $\alpha$  in equation (1) was constant; it fell off rapidly at lower pressures, indicating clearly that the positive ions were disappearing by recombination rather than by arrival at the collector. Over the constant range in which the experiments were made the proportion arriving at the collector must have been constant, but it is difficult to be certain that it was unity; and if it was not, the values of  $n_1/n_2$  would be too high. Apart from this vessel, the highest value obtained was 2.5 on the flat part of a good curve; but higher values up to 5.4 were often obtained when the discharge was first started. The first few observations were often irregular, and usually above the remainder of the curve; what is their significance cannot be determined until the cause of variation is known.

### *The Thermal Evolution.*

11. Closely connected with the influence of the walls is the evolution of gas when the vessel is heated. We have attempted to study this evolution in detail; if intelligible results could be obtained, they might give much information concerning the nature of the absorption. We propose later to report on these experiments more fully; at present the results are chaotic and unintelligible. But one important fact is clear. There is no definite amount of gas that can be liberated by baking; the results of increased temperature resemble rather the establishment of a vapour-pressure than the progress of a continuous reaction.

If a vessel exhausted for several hours while maintained at (say) 360° C. is sealed off, allowed to cool, and then maintained at (say) 100°, the pressure increases, rapidly at first and then more slowly, until after a period of many hours (say 100) an equilibrium pressure is attained which does not increase with time. If it is now cooled, the

pressure falls, rapidly at first and then more slowly; the original pressure at room temperature is not usually reached; there is some permanent evolution. If the heating and cooling are repeated, an equilibrium pressure, somewhat higher than before, is attained, and the final pressure reached on cooling is again somewhat greater. If, after the original heating at  $100^{\circ}$ , the temperature is raised to  $200^{\circ}$  C., the pressure will again reach equilibrium at a higher value. Permanent increases are produced by alternate heating and cooling; but there is some reason to believe that even this permanent evolution decreases as the cycle is repeated, and that finally a state would be obtained in which the equilibrium pressure is determined only by the temperature.

These features are characteristic of all the well-exhausted vessels we have examined (except one, wholly anomalous and unexplained, which gave no change of pressure with temperature), whether or not gas has been made to disappear in them by the process studied here. In fact, we have never been able to satisfy ourselves that the absorption of gas by the discharge had any effect on the thermal evolution; it is certainly not true that, if two vessels are exhausted in apparently the same way and gas is absorbed in one and not in the other, that in which gas has been absorbed will always give the greater rise of pressure with temperature. In other words, we have no evidence that the gas absorbed by this process is capable of being restored by heating to any temperature under  $300^{\circ}$  C.

Nor does there appear to be any temperature below this limit at which the electrical absorption ceases; if the discharge is passed in the warm vessel absorption occurs, but at a smaller rate than at room temperature.

In the course of the experiments on "residual gas" many observations were made in which gas was alternately liberated by heating and absorbed by the discharge in the same closed vessel. On each repetition of the cycle the equilibrium pressure attained at any temperature during the baking decreased, and the value of  $n_1/n_2$  at any pressure during the absorption increased. The cycle on the whole tended to remove gas. If the facts are to be represented in terms of vapour-pressure, the relation between thermal evolution and electrical absorption can be summed up in the statement that the discharge progressively decreases the vapour-pressure of the vessel.



## COMPARISON WITH PREVIOUS WORK.

12. Before discussing our results, it will be well to compare them briefly with those of Hughes (*loc. cit.*), who alone appears to have made measurements of the same nature. Hughes compared the number of molecules absorbed with the number of collisions between molecules and ionizing electrons, and not with the number of ions formed. With the anode voltages which he used, probably about one collision in every four resulted in ionization (see below, p. 578); accordingly his "*b*" will be comparable with our  $n_1/n_2$  if the former is multiplied by 4. It then appears that the greatest value of  $n_1/n_2$  which he observed was about 0.7. This is consistent with our results, for his vessel was very small; however, since the walls were cooled and under bombardment by electrons, and since he was using hydrogen, we should have expected him sometimes to observe higher values. He finds a progressive decrease of the rate of absorption with increase in the initial pressure, which is what we find when the anode forms a considerable fraction of the walls of the vessel. He finds more variation with the anode voltage than we do; but since his absorption was not nearly independent of the pressure, his observations on this point are not comparable with ours. He finds less difference between nitrogen and hydrogen than we find. We agree with his observations that there is no appreciable absorption unless there is ionization. We have found no trace of the anomalous clean-up which he found in nitrogen, but our vessels with oxide-coated filaments were not cooled in liquid air.

## DISCUSSION OF THE RESULTS.

*Absorption and Ionization.*

13. We have now summarized those observations which we have been able to reduce to some kind of order; the proportion reducible to order would probably have been greater if a clue had been discovered earlier. An attempt to explain them must answer two main questions. The disappearance of the gas is doubtless due to some reaction between the molecules of the gas and of the solid walls, resulting in the formation of stable complexes attached to the walls. We have to determine what is the nature of this reaction and what is the state of the molecules of the gas which enables them to undergo this reaction. It is just possible that this second question does not arise, that the effect of the discharge is wholly on the walls, and that the

molecules of the gas which disappear are in their normal state ; but all the evidence seems against this view, and we do not propose to consider it further.

We shall start with the second question ; and we shall pay attention primarily to the absorption curves of the form shown in figs. 1 and 4 which are obtained with nitrogen and carbon monoxide. For though an explanation of these curves would not cover the whole ground, we feel convinced that they represent the phenomena in their simplest form, and that the other absorption curves involve complicating factors which are best left out of account in a preliminary survey.

At first sight, we might be inclined to adopt a very simple hypothesis. It might be supposed that ionization causes absorption, because the positive ions themselves adhere to the walls.

But this, the most natural theory, is open to the gravest objection. For if the positive ions disappear as positive ions, they must all disappear on the collector ; for the collector is the only solid surface they hit while they are positive ions ; when they leave it they are certainly uncharged, because their charge has passed through the galvanometer. This argument is unaffected if the ions never really take up an electron, but merely attract one to the surface of the electrode ; if the ion subsequently left the electrode, this electron would be set free in the electrode. But, from the time of the earliest experiments on this subject, all the evidence has been against the absorption of the gas on the electrode which received the positive ions ; it has always been much more probable that it is absorbed on any surface exposed, almost irrespective of its charge. To this evidence we have added.

In one experiment, the collector was a squirrel-cage lamp filament. After a considerable amount of gas had been cleaned up in this vessel, the collector was heated to more than  $2000^{\circ}$  K. for a few minutes, but no considerable fraction of the gas was restored. The small increase of pressure which occurred could well be attributed to the heating of the walls by the incandescent filament. Conversely, in other experiments a portion of the wall of the vessel was cooled in liquid air. An increase in  $n_1/n_2$  was thereby produced, even if this part was the anode or was of bare glass and insulated. Again, in one vessel the wall of the vessel was silvered in two separate halves. Both halves were initially bombarded with electrons till no more gas was evolved. During the absorption of the gas, one of the halves

was kept at a small positive potential, the other was the collector and received all the positive ions. After the gas had been absorbed, one of these was made the anode of the discharge and bombarded with electrons; gas was then evolved (*cf.* § 7). If the gas had collected on the collector, the evolution should have been greater if that half was bombarded; but no difference between the two halves could be discovered.

Lastly, there are the experiments of § 7, when the small electrode was the collector. It would doubtless help to explain some of the facts if it could be supposed that the gas was always absorbed on the collector, and that the difference in the maximum absorption, according as the collector was the large or the small electrode, was due to a difference in the material of which they were composed. But the quantity of gas that could be absorbed with the small electrode as collector was far greater than would cover that electrode completely with a monomolecular layer of gas, whereas in the experiments of p. 569 the absorption practically ceased long before a monomolecular layer was completed. This difficulty is still more marked in the experiments with the lamp filament as collector; the area of this electrode was even smaller than that of the spiral surrounding the cathode. And the possibility that in this experiment all the positive ions were not reaching the collector makes the difficulty even worse: for, on the theory that we are discussing, if the ions do not reach a solid electrode, but are neutralized by recombination, they should not disappear.

None of these arguments is entirely conclusive by itself, but, taken together, they seem to us to make it almost impossible to maintain that the absorption of the gas is due directly to the absorption of the positively-charged ions. Alternative theories must be considered; but before proceeding to them, it will be well to notice some questions which will arise whatever theory is adopted.

#### *The Form of the Absorption Curve.*

14. First, is it certain that all the positive ions arrive at the collector? May not some part of the bare insulated glass be negatively charged and receive positive ions, which, perhaps, are continually neutralized by a small fraction of the electronic stream? We do not believe that there is any appreciable action of this sort. In vessels of type B, the bare glass was reduced to the minimum necessary for insulation, and its effect can hardly have been appreciable. Most of our results were obtained with vessels of this type,

and are therefore unaffected by the possibility suggested. Moreover, no material difference could be found between the observations in such vessels and in those of vessels of type A, where there was a large area of bare glass, or in those of type B with only part of the walls silvered. Again, the positive-ion current was always saturated and did not increase with  $V_g$ . Lastly, exploration of the charges on the bare glass by various methods showed that the surface of this glass was always very nearly at the potential of the cathode, and therefore less likely to receive positive ions than the negatively-charged collector.

Second, what is the significance of the form of the absorption curve, and how can values of  $n_1/n_2$  occur which are greater than 1? If the theory that we have just discussed were true,  $n_1/n_2$  could be greater than 1 only if the positive ions collected to themselves neutral molecules either before or after they were absorbed on the walls. The form of the absorption curve might suggest that the formation of complexes of primary positive ions and neutral molecules occurred before absorption, and that the rapid falling-off of the absorption at low pressures was due to a diminution of the frequency of collisions at which such formation can take place. But the falling-off occurs at pressures too low for this explanation to be probable; the curve is straight far below the pressures at which the chance of a collision between a neutral molecule and a positive ion on its way to the collector has begun to decrease rapidly. We believe that the form of the curve at the lowest pressures is due simply to the partial counteraction of the absorption by one or more of the evolutions discussed on p. 556. When the pressure becomes low,  $dp/dt$  necessarily falls unless  $i_a$  is very greatly increased; the ratio of the thermal evolution to the electrical disappearance is no longer inappreciable, and  $n_1/n_2$  appears to decrease. Confirmation of this suggestion was sought in observations of the thermal evolution when the fields were removed and the discharge stopped; it is difficult to obtain great accuracy in the comparison, but in some cases at least the residual thermal evolution measured in this way was quite sufficient to account for the falling-off of the curve; again, the falling-off occurs at lower pressures when the thermal evolution is small. There is also the electrical evolution from the small anode to be taken into account. In a general survey of the observations we can find no evidence that, if all evolution could be suppressed,  $n_1/n_2$  in nitrogen and carbon monoxide would not be nearly constant down to the lowest pressures.

If that is so, reactions between molecules of the gas, when they are in the gaseous state, cannot be responsible for the main part of the absorption of nitrogen and carbon monoxide. If reactions between gaseous molecules are a primary cause of absorption, they must take place between free molecules and those already condensed on the surface on the walls. On the other hand, if, in these gases,  $n_1/n_2$  does increase slowly but regularly with the pressure (and we have never been able to decide whether it does or does not), this increase may be due to reactions between free molecules which play a secondary part in the absorption. In CO we know already of a reaction which might play such a part \*. But even here the apparent decrease as the pressure falls may be due to the partial counteraction of the absorption by an evolution independent of the pressure, *e. g.* an electrical evolution from the anode of small area. In those gases, *e. g.* hydrogen and "residual gas," which show much more definitely a steady increase in  $n_1/n_2$  with pressure, the influence of these reactions must be more important; but since, even here, they cannot be the sole cause of absorption, it is permissible and probably wise to discuss the matter first as if they did not occur.

#### *Absorption and Monatomic Molecules.*

15. But what alternative theories can be offered? If the particles of the gas are uncharged at the time of their absorption, the state which favours absorption must be one associated with ionization, but not ionization itself. An obvious suggestion is that the molecules are resolved by ionization, that in nitrogen and hydrogen the state in question is the monatomic state, and in carbon monoxide either the elementary state or some state of less saturated combination. But there are objections here also. Though it is certain that some molecules are resolved on ionization, it is equally certain that not all are. Our experiments on carbon monoxide (*loc. cit.*) indicated strongly that most of the molecules were unresolved; for nitrogen still more definite evidence is available from the interesting work of H. D. Smyth †. His results show that, when the speed of the ionizing electrons is below 350 volts, only about one-tenth of the ions are atomic; the rest are molecular. If, then, we are to explain the disappearance of more molecules than are ionized, we must suppose that the active atoms or

\* Phil. Mag. xlii, p. 227 (1921).

† H. D. Smyth, Proc. Roy. Soc. A, civ, p. 121 (1923).

resolved molecules, after being absorbed, can collect around them other neutral molecules which happen to come into their neighbourhood. Such an action is not intrinsically improbable; but, if we have to account for values of  $n_1/n_2$  at least equal to 3, while there is no evidence that the number of molecules primarily activated is more than a tenth of the ions, the magnitude of the complexes that must be involved in absorption become alarmingly large; at least 30 atoms must be concerned in them.

Further, if this theory is correct and Smyth's conclusions are reliable (as they appear to be), there should be a great increase in the value of  $n_1/n_2$  when  $V_a$  is greater than 400 volts, because the ratio of atomic or molecular ions is greatly increased at such high voltages. The significance of Smyth's work for our observations was only realized when the experiments were nearly completed, and there has not been time to carry the observations of fig. 2 fully to higher values of  $V_a$ . But enough observations have been taken to show that there is no considerable difference between the values of  $n_1/n_2$  at  $V_a=300$  and  $V_a=500$  such as would be expected if the resolution of the molecule were the determining factor in absorption. While, therefore, the evidence against this theory is not quite so strong as against the first which was noticed, the available evidence seems contrary to it; other alternatives must be investigated.

#### *Absorption and Partial Ionization.*

16. A third alternative is that the state of the molecules which favours absorption is excitation or partial ionization—that is to say, a quantum state higher than the normal but lower than ionization. There is much evidence\* that excitation may favour the formation of complexes or definite chemical compounds, such as must be involved in the disappearance of material from the gaseous state. Moreover, the theory is not inconsistent with the values of  $n_1/n_2$  that have been found or with their relation to  $V_a$ . If a vessel of type B is used with the silvered wall as anode, the distance travelled by the electrons is known approximately, and the average number of ions made by each electron can be compared with the number of collisions it must make if the dimensions of the molecules are taken from the kinetic theory. As the following table shows (in accordance with what is already known), the number of ions per collision is considerably less than unity, and does not vary very rapidly with  $V_a$  over the relevant range. If, as seems probable,

\* See e. g. K. T. Compton, *Journ. Opt. Soc. Amer.* vii. p. 955 (1923).

every collision results either in excitation or ionization, the ratio of molecules excited to those ionized must be considerably greater than unity ; it is therefore possible to explain the occurrence of values of  $n_1/n_2$  greater than unity without introducing complexes involving more than one molecule of the gas.

$V_a$ (volts).	Ions per collision.
100 .....	0.179
200 .....	0.208
300 .....	0.236
400 .....	0.257
500 .....	0.271

But there are some difficulties. First, it is not possible to explain by the figures just given the highest values of  $n_1/n_2$  observed. But there is some doubt about values greater than 3 ; moreover, they have always been observed when collisions between molecules of the gas were relatively frequent and the formation of complexes in the gas is not excluded. Second, perhaps the figures suggest a greater variation of  $n_1/n_2$  with  $V_a$  than has been found. But here Smyth's results (*loc. cit.*) show clearly that the mere determination of ions per collision does not give full information as to the relative frequency of different types of ionization. Third, on this theory there should be some absorption when  $V_a$  is less than the ionization potential. We have never been able to detect such absorption ; but since the absorption decreases rapidly with the voltage as the ionization potential is approached, it is just possible that it may have escaped detection. Last, the experiments of Wien and others\* indicate that the duration of the excited state is of the order of  $10^{-7}$  sec. ; in such a period molecules excited throughout most of the vessel would not have time to reach the walls ; and if they reach the walls in the normal condition, it is not easy to explain their disappearance. But perhaps this difficulty can be overcome by means of Compton's theory of the diffusion of radiation, and therefore of the excited state. The molecules that disappear may not be those originally excited, but those excited in immediate proximity to the walls by radiation due to the original excitation.

To sum up, the constancy of  $n_1/n_2$  for variations of the pressure and of  $V_a$ , together with the absence of appreciable absorption when  $V_a$  is less than the ionization potential, suggests at first sight that the absorption of the gas is a direct consequence of ionization, and that the ions are absorbed. But this explanation seems impossible, because the ionized molecules remain ionized only during their

\* W. Wien, *Ann. d. Phys.* lxxiii. p. 483 (1924), etc.

passage to the collector, and because they are not absorbed on the collector. Both the alternative theories are equally open to serious objections. The theory directly suggested by the facts is that molecules are absorbed when they have been ionized and subsequently neutralized by contact with the collector, that they are absorbed indifferently all over the surface of the vessel, and that after absorption they can collect round them neutral molecules and thus secure the absorption of more molecules than are ionized. But this theory is not easy to reconcile with what is known of ionization or atomic structure.

*The Nature of Absorption.*

17. The second problem to be solved by any complete theory is the nature of the reaction between the gaseous molecule and the wall which is the immediate cause of absorption. Here we have even fewer and less definite suggestions to offer. The main difficulty arises from the apparent independence of the absorption of the chemical nature of the absorbing surface. If the absorption is "chemical," then whether it depends upon "primary" or "secondary" valencies, and whether it is more nearly allied to homopolar or heteropolar chemical combination, a definite influence of the material of the walls would be expected, and more difference than we have found between gases so chemically different as nitrogen and carbon monoxide. This last point is important; for even if it is thought that the absorption does not depend on the nature of the walls because it is really substantially the same in all gases (for instance, if they are always covered with a layer of gas), there is no doubt about the difference of the gas. It may be urged that a close similarity between nitrogen and carbon monoxide is to be expected if the absorption is purely "physical," and closely allied (*e. g.*) to the absorption by charcoal; but it may be replied that even here an influence of the nature of the walls is to be expected, and that the greater absorption of hydrogen and the far smaller absorption of argon show no analogy to this kind of absorption.

The only contribution that we can make to a solution is an indication that it is only a fraction of the whole surface of the vessel that can absorb. The experiments on fatigue show that the absorption decreases far more rapidly than the fraction of the surface that would remain uncovered if the absorbed gas were uniformly distributed. Again, the high values of the initial absorption in some experiments suggests that there is a part of the surface, soon used up, in an abnormally active condition. The special activity would



have to consist in an ability to absorb molecules less highly activated than those which adhere to the normal active surface. On the other hand, the recognition of inactive patches, and of the possibility that an activated molecule may not be absorbed because it strikes an inactive patch, increases the difficulty, already grave, of explaining values of  $n_1/n_2$  greater than unity.

The influence of electron bombardment may provide a clue, though we cannot find it at present. It is easy to understand why such bombardment should liberate absorbed gas; for whatever may be the active state of the absorbed molecule, it is likely to be disturbed by the impact of electrons. But it is difficult to understand why the maximum absorption on a bombarded surface should be greater than on one that is not bombarded, and why such a maximum should occur between two stages in which the absorption is less than it is in the absence of bombardment. Unless it can be held that, when the small electrode is the collector, the gas is absorbed on that electrode piled up many molecules deep, it seems almost necessary to suppose that the absorption is different according as electrons are or are not striking the surface, and that the absorption which takes place in their absence is more easily reversed by the bombardment than that which takes place in their presence. But we can suggest no explanation of such a difference.

Finally, we would revert once more to the possibility of reactions between the molecules of the gas. It is highly probable that such reactions may occur; indeed, our previous work on carbon monoxide shows that in this gas they must occur; but it is highly improbable that the formation of complexes in such reactions is an important factor in absorption. To the reasons for this view that we have already given, we would add that positive ray analysis provides no evidence that complex molecules are often formed in the process of ionization; and that, even if they were formed in the gases that have been investigated, there is little likelihood that they would form solids and so cause directly the disappearance of the gas. On the other hand, if there is really a steady increase of electrical absorption with pressure in hydrogen (it is doubtful because of the absorption which takes place in the absence of the discharge), the normal molecules must be concerned in it in some way. If the theory of the absorption of excited molecules could be accepted, the effect of pressure might be attributed to secondary excitation due to radiation emitted under primary excitation. But the facts are here too uncertain to form the basis of any theory.

LVII. *The Dielectric Properties required for Maxwellian Radiation.* By A. PRESS \*.

*Summary.*

QUITE apart from the two curl equations symbolizing Maxwell's Electromagnetic Theory, a consideration of generalized mechanics leads to a differentiation between the  $\mu_r$  and  $k_r$  coefficients for radiant manifestations such as light or Hertzian waves on the one hand, and the  $\mu_s$  and  $k_s$  coefficients for zero frequency conservative systems on the other hand. Indeed, the requirement is that in every case, as experiment shows, the  $k_s$  and  $\mu_s$  coefficients should be larger. Then, taking note of Maxwell's curl equations it is proved that the electrical refractive index should not be expected to agree with the optically determined refractive index. The above two considerations necessarily lead to a modification of our concepts of self-induction and capacity coefficients for radiant systems.

*The Activity Equations.*

In a generalized mechanical system the activity  $A$  is defined as the result of multiplying the generalized force by a corresponding generalized velocity. In electrodynamics such force is the electrical intensity  $E$ , whereas the generalized velocity is the time-rate of change of generalized displacement  $D$ . Thus the activity per unit volume  $d\tau = dN \cdot dS$  is given by

$$A_e = \frac{1}{d\tau} \left\{ E \cdot dN \cdot \frac{dD}{dt} \cdot dS \right\} = E \cdot \frac{dD}{dt},$$

with  $dN$  as the element of the unit normal  $N$  and  $dS$  as the element of area normal to  $N$ . Thus for a simple sinoidal variation of the quantities involved no real activity can possibly result if the generalized displacement  $D$  is taken to be in time phase with the impressed generalized force.

*Consequences of Time-Variations Harmonically Considered.*

For generality let it be assumed that :—

$$\begin{aligned} E &= E_1 \sin pt + E_2 \cos pt, \\ D &= D_1 \sin pt + D_2 \cos pt. \end{aligned}$$

\* Communicated by Prof. T. J. Schwatt, Ph.D.

Then we have that

$$A_e = p \left[ \{ E_2 D_1 \cos^2 pt - E_1 D_2 \sin^2 pt \} + (E_1 D_1 - E_2 D_2) \sin pt \cdot \cos pt \right].$$

The term involving  $\sin pt$ ,  $\cos pt$  cannot give rise to any real time integrated activity, since the expression changes sign with the time. Yet by simple trigonometry the term  $\{ \}$  can be transformed, and then

$$A_e = p \left[ (E_2 D_1 - E_1 D_2)_r \cos^2 pt + E_1 D_2 \cos 2pt + \frac{1}{2} (E_1 D_1 - E_2 D_2) \sin 2pt \right].$$

Whether any real activity results therefore depends on whether the expression  $( )_r$  is greater than zero or not. That is, for real consumption of energy the following inequalities must subsist :—

$$E_2 D_1 > E_1 D_2 ; \quad D_1/E_1 > D_2/E_2.$$

Indeed with

$$E_2 D_1 - E_1 D_2 = 0,$$

or what amounts to the same thing

$$E_1/D_1 = E_2/D_2,$$

there can only be a completely wattless consumption of energy. Thus for true radiation it is seen that the usual expression

$$D = kE$$

cannot obtain with  $k$  as a real (non-operational) number for the proportionality factor.

For the magnetic case equally and quite independently we must have, with

$$H = H_1 \sin pt + H_2 \cos pt$$

$$B = B_1 \sin pt + B_2 \cos pt,$$

that for real watt consumption

$$B_1/H_1 > B_2/H_2.$$

Therefore  $\mu$  cannot be real but must be time-operationally complex.

#### *Activity Requirements for Progressive Wave of Displacement Flux.*

The inequalities above have been introduced to emphasize the time-phase factors only. A better form would be to set

forth the progressive and stationary wave-components of the generalized displacement. In this manner the radiant energy is localized in the voluminal displacement wave carried forward. Thus let

$$E = E_s + E_p,$$

where  $E_s$  is the stationary wave-component of force (as in a non-radiating condenser action) and  $E_p$  represents that component of the impressed force giving rise to the progressive (or radiant) wave-component. In the same way we have

$$D = D_s + D_p.$$

If now we set

$$\phi = f(x, y, z),$$

then it is proper to take

$$E = E_s \sin pt + E_p \sin (pt + \phi),$$

$$D = D_s \sin pt + D_p \sin (pt + \phi),$$

with the understanding that it is  $E_s$  that produces  $D_s$ , etc.

Investigating afresh the activity relations we find

$$\begin{aligned} A_s &= (E_s + E_p)(dD_s/dt + dD_p/dt) \\ &= \left( E_s \cdot \frac{dD_s}{dt} + E_p \cdot \frac{dD_p}{dt} \right) + \left\{ E_p \cdot \frac{dD_s}{dt} + E_s \cdot \frac{dD_p}{dt} \right\}. \end{aligned}$$

It is evident that the terms in  $\{ \}$  can produce no real component of loss. With respect to the terms in  $\{ \}$  we have

$$\begin{aligned} \{ \} &= p [\cos \phi \cdot \sin pt \cdot \cos pt (E_p \cdot D_s + E_s \cdot D_p)_1 \\ &\quad + \sin \phi \cdot (D_s E_p \cos^2 pt - D_p E_s \cdot \sin^2 pt)_2]. \end{aligned}$$

By trigonometry, however, it again turns out that

$$(\ )_2 = (E_p D_s - E_s D_p)_2 \cdot \cos^2 pt + E_s D_p \cdot \cos 2pt.$$

The real activity therefore depends on whether  $(\ )_2$  gives the following inequalities

$$E_p D_s > E_s D_p : k_p = \frac{D_p}{E_p} < \frac{D_s}{E_s} = k_s,$$

and similarly for the magnetic case where with

$$H = H_s \sin pt + H_p \sin (pt + \psi),$$

$$B = B_s \sin pt + B_p \sin (pt + \psi),$$

$$H_s B_p < H_p B_s ; \mu_p = \frac{B_p}{H_p} < \frac{B_s}{H_s} = \mu_s.$$

Conceiving then, for convenience, of a new mathematical operator  $R$  such that when acting on the activity expression  $A_e$  it gives the real component of the energy rate consumption, we have

$$RA_e = p \sin \phi \cdot (E_p D_s - E_s D_p) \cos^2 pt.$$

The latter expression can be transformed by means of the relations derived, and it follows :

$$\begin{aligned} RA_e &= p \sin \phi \cdot E_p D_p (E_s/E_p) (k_s/k_p - 1), \\ &= p \sin \phi \cdot E_p D_p (D_s/D_p) (1 - k_p/k_s). \end{aligned}$$

For the magnetic case correspondingly we have

$$\begin{aligned} RA_m &= p \cdot \sin \psi \cdot H_p B_p (B_s/B_p) \left(1 - \frac{\mu_p}{\mu_s}\right), \\ &= p \cdot \sin \psi \cdot H_p B_p (H_s/H_p) \left(\frac{\mu_s}{\mu_p} - 1\right). \end{aligned}$$

The magnitude of the radiation is therefore seen to depend on the relative strength of both fields stationary and progressive at any point. The above separate developments be it noted are quite independent of the two curl equations of Maxwell.

*The Differential Equation of Maxwellian Radiation.*—If the developed flux coefficients are introduced into the expressions for the two displacement expressions, we have

$$D = k_s E_s + k_p E_p,$$

$$B = \mu_s H_s + \mu_p H_p.$$

Substituting the latter in the fundamental curl equations of Maxwell, we really have that

$$\text{curl } E = \text{curl } (E_s + E_p) = -dB/dt = -d/dt(\mu_s H_s + \mu_p H_p),$$

$$\text{curl } H = \text{curl } (H_s + H_p) = dD/dt = d/dt(D_s + D_p).$$

Assuming, for example, that the curl (line integral per unit of area) of  $dD/dt$  can be separated out into its two components independently, we have

$$\text{curl } H_s = dD_s/dt ; \text{curl } H_p = dD_p/dt,$$

$$\text{curl } E_s = -dD_s/dt ; \text{curl } E_p = -dD_p/dt.$$

In this manner, therefore, the following two resultant

equations will follow

$$\nabla^2 D_s = \mu_s k_s \frac{d^2 D_s}{dt^2}$$

$$\nabla^2 I_P = \mu_p k_p \frac{d^2 I_P}{dt^2}$$

Yet must we have

$$\mu_s k_s > \mu_p k_p,$$

which has important physical consequences.

### *Relation of Dielectric Constants to Index of Refraction.*

It is a well-known fact from experiments with light waves for determining the index of refraction that the dielectric constant  $k$  always comes out smaller than when determined by the charged condenser method. Since light is a radiation phenomenon, and on the assumption of Maxwell it is electromagnetic, the value of the light velocity  $c$  is given by

$$c = \frac{1}{\sqrt{\mu_p k_p}}.$$

Yet for the electrical condenser experiments, where radiation effects are not emphasized, to say the least, it is not proper to take the right-hand term as  $1/\sqrt{\mu_s k_s}$ . The relative value of the refractive index  $i$  should be given by

$$i = \sqrt{\frac{\mu_p' k_p'}{\mu_p k_p}}.$$

The work of M. C. Gulton, *Comptes Rendus*, 1900, cxxx, p. 119, is therefore of exceptional interest. He found that the electrical refractive index for ice, for example, decreased progressively with larger and larger wave lengths, approaching more and more the value found by Fleming for a dry prism of ice when subjected to Hertzian waves. Quite a large table of values of  $i^2$  and really  $k_s$  are given in Fleming's 'Principles of Wireless Telegraphy.'

Finally, it must be said that since the self-induction coefficient  $L$ , and the capacity coefficient  $C$  are dependent on the effective  $\mu_s$  and  $k_s$  values, our conceptions of the constants are naturally altered in the light of the above inquiries. As for the power factor of an oscillating system, it is seen it must be always less than 50 per cent.

Chevy Chase, Md., U.S.A.

June 7, 1924.

LVIII. *Spectrophotometry of the Zeeman Effect in very weak Magnetic Fields.* By WALI MOHAMMAD, Ph.D. (Göttingen), M.A. (Punjab), B.A. (Cantab.), Professor of Physics, Lucknow University\*.

### 1. Introduction.

**I**N order to study the distribution of intensity in a spectrum line when subjected to a very weak magnetic field and before the line is resolved into its components, the spectrophotometry of a photogram produced by an Echelon Grating Spectroscope was undertaken and the following arrangements adopted :—

### 2. Source of Light.

A source capable of giving sharp, fine, and bright lines is absolutely essential, and for this purpose an arc in vacuum produced by means of a Wehnelt oxy-cathode and an anode consisting of the given substance was used. The discharge-tube was similar to the one described previously by the author†, and consisted of a lime-coated cathode heated to incandescence by means of an electric current and an anode of zinc. A voltage of 220 volts was applied between the cathode and the anode, and the metal placed at the anode was made to evaporate and to emit light. This arrangement was virtually an arc in vacuum—the pressure being less than 0.01 mm. Hg. The zinc lines were chosen for investigation, as they had been proved to be without any satellites and had no complex structure and were sharply defined. By maintaining the current constant, the rate of the evaporation of the metal and consequently the intensity of the emission could be maintained uniform for considerable periods.

### 3. Spectroscope.

The spectroscope used was an echelon grating made by Hilger and consisted of 35 plates. This was used in conjunction with a monochromator of the constant deviation type. Its resolving power lies between 285,000 and 665,000 for the Fraunhofer lines A and H respectively, and the limit of the wave-length difference capable of being resolved is 0.027 and 0.006 Å respectively.

\* Communicated by the Author.

† Wali Mohammad, *Astrophysical Journal*, xxxix. p. 185 (1914).

#### 4. *Magnetic Field.*

The magnetic field was applied by placing the above mentioned discharge-tube containing the oxy-cathode and the anode between the poles of an electromagnet with adjustable poles, and capable of producing a field of about 7000 gauss when a current of 15 amp. was sent through it and when the distance between the poles was about 35 mm.

#### 5. *Spectrophotometer.*

The photometer used was one constructed by Professor J. Hartmann\*. In this instrument, the depth of tint at any point on the photographic plate is compared with that on a standard plate, and the place which has the same depth of tint is noted.

The instrument measures with high precision the density of a restricted area of the photographic image and can, with care and patience, be used to show the variation of this density from point to point.

#### 6. *Sensitiveness of the Arrangement.*

Most of the Zeeman effect determinations have been made in very strong magnetic fields, and observations in weak fields are very few. The reason for this is obvious. The separation of the lines is so small as to require an instrument of very high resolving power to detect it. If the line is not a sharp one, its study offers further difficulties.

With the arrangement described above, the author not only detected but measured in the case of certain lines of cadmium the magnetic resolution in fields as weak as 300 gauss, and the author is not aware of any other measurements in fields much weaker than the above; the lowest magnetic field in which the Zeeman effect appears to have been observed is 535 gauss, observed by O. V. Baeyer† by means of a Lummer-Gehrcke plate.

#### 7. *Photograms.*

For photographing the lines Wratten and Wainwright's isochromatic plates were used, and several photographs were taken on the same plate in close proximity to one another. The magnetic field was gradually varied and was practically proportional to the current flowing in the coils, being 0, 290, 581, and 871 gauss respectively for currents of 0, 0.5, 1, and 1.5 amp.

\* Hartmann, *Zeitschr. f. Instrumentenk.* xix. p. 97 (1899).

† Baeyer, *Verh. d. Deutsch. Phys. Ges.* viii. (1906); *ibid.* x. (1908).



8. *Sources of Error.*

Koch\*, in an exhaustive study of the probable sources of errors in the photometry of spectrum lines, has mentioned no less than ten different sources, the most important among them being: the inhomogeneity of the photographic plate, the temperature variation during exposure, the diffusion of light in the photographic film, and the influence of the width of the slit. Apart from these there are other important sources of error likely to affect the experiments. These are:—

(a) The polarization impressed upon light which traverses fine slits. This phenomenon, originally noticed by Fizeau, has been further investigated by Zeeman †, who has shown that polarization caused by a too narrow slit gives rise to errors in determinations of intensity of components, and also to apparent shifts and dissymmetrical resolutions of spectrum lines with originally symmetrical distribution of light. He has shown that a quartz plate introduced before the slit of the spectroscopic, giving a rotation of the plane of polarization of  $45^\circ$ , eliminates this source of error.

(b) The effect of the position of the echelon grating. The echelon grating may be used in either of the three positions:—

- (1) When two neighbouring orders are of equal intensity.
- (2) When only one bright single line is visible.
- (3) Positions intermediate between these two with two lines visible but of unequal brilliancy.

By a slight rotation of the echelon about a vertical axis any of the conditions above mentioned can be secured, and therein lies the risk of changing the intensity of the lines and of getting dissymmetries.

The intensity curve of a fine spectrum line without a magnetic field shows the distribution to be quite symmetrical and similar to what may be expected on theoretical grounds. The agreement between the intensity curve observed by the author and that given by Koch ‡ in his researches on spectrophotometry is very close indeed. This shows that none of the above sources of error was present.

9. *Results.*

The red zinc line  $\lambda = 6364$  was chosen for observation, and the curves of intensity variation in magnetic fields of varying

\* Koch, *Annalen der Physik*, xxxiv. p. 377 (1911); xlii. p. 1 (1913).

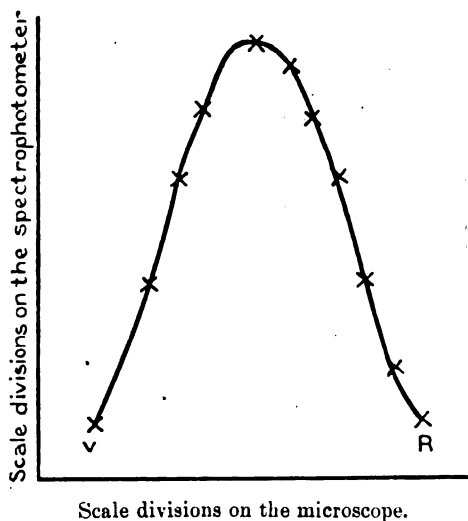
† Zeeman, *Proc. Roy. Acad. Amsterdam*, xv. pp. 599-601.

‡ P. P. Koch, *Annalen der Physik*, xxxiv. p. 377 (1911).

strength are given. The line has been found to yield a normal triplet in the magnetic field. The middle component was removed by means of a Nicol's prism.

The curves show that even with the weakest magnetic field employed, the line shows two components not quite symmetrical either in intensity or in position, and this dissymmetry is maintained even when the field strength is increased.

Fig. 1.



$H = 0$  Gauss.

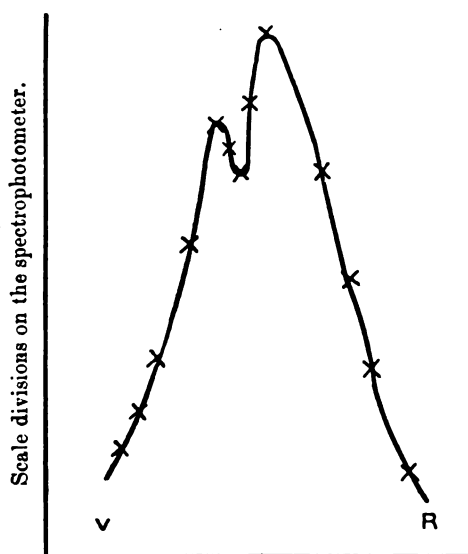
### 10. Discussion.

Not long after the discovery of the Zeeman effect and its explanation on the electronic theory of Lorentz, doubts were raised regarding the symmetrical distribution of intensity and distances of the components, and Zeeman and Voigt\* predicted certain kinds of dissymmetries. According to Voigt normal inverse triplets in *weak* magnetic fields exhibit a dissymmetry of the following nature:—

The outer component on the side of the *red* has the greater intensity, and the component on the side of the *violet*

\* Voigt, 'Magneto- und Electro-optik.' Voigt, Graetz's 'Handbuch der Elektrizität und des Magnetismus.'

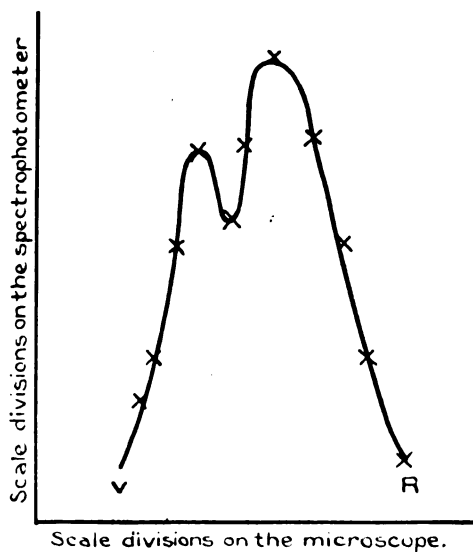
Fig. 2.



Scale divisions on the microscope.

$H = 290$  Gauss.

Fig. 3.

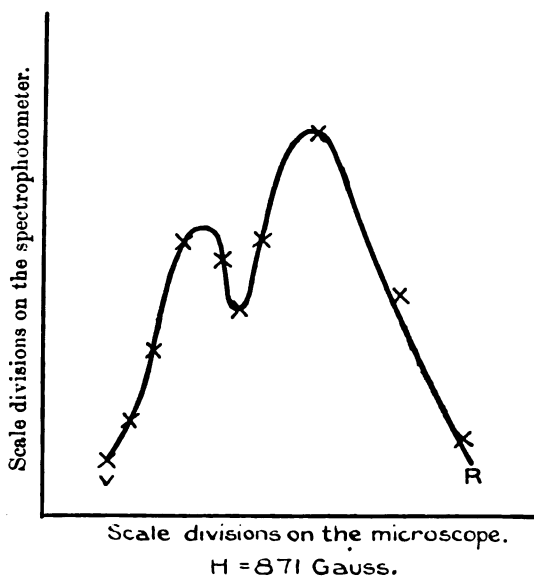


Scale divisions on the microscope.

$H = 581$  Gauss.

will be at the greater distance from the original line. In weak fields, these dissymmetries will preponderate with observation perpendicular to the field, disappearing, however, in strong fields. Such dissymmetries have been proved to exist in many cases, and the spectrophotometric results given above appear to confirm the above-mentioned observations.

Fig. 4.



A dissymmetry of this nature cannot be explained on the simple electronic theory, but is probably due to one of the following causes :—

(a) It may be due to the coupling between electrons with different frequency. The interesting theory of the anomalous Zeeman effect developed by Voigt fully explains the sign and the nature of the dissymmetry observed above, and is probably the only theory put forward so far which not only explains the observed facts but even predicts phenomena which have later on been verified by observations. According to this theory, the displacements are proportional to the square of the strength of the magnetic field, but as the field becomes stronger the displacements tend to be proportional to the field strength. Moreover, the intensity of the component

$\propto R^2$

on the side of the violet will be at a greater distance from the original line.

(b) It may be due to the modification of the quasi-elastic forces by the magnetic field, or a change in the structure of the radiating particles under the influence of the magnetic field. This view was adopted to explain the well-known Paschen-Back effect and was utilized by Voigt in developing his theory.

(c) The dissymmetry may be due to the interaction of the magnetic and electric forces. Zeeman\* has proved experimentally, at least in cases investigated by him, that the magnetic force is solely responsible for a dissymmetry of such nature and that the electric force is not operative. It is true that such dissymmetries have been observed in flames where the electric forces are not operative, but there is no doubt that in an arc (or a spark) the conditions are certainly complicated and probably the Stark effect has something to do with such dissymmetries.

It may be remarked that the Bohr application of the quantum theory has not been able so far to explain some of the complicated but extremely regular magnetic resolutions. Sommerfeld, using Bohr's atomic model, has applied the quantum theory to account for the normal Zeeman effect, but he has neglected the squares of the magnetic field which are probably responsible for the dissymmetries of the kind noted above. He† has recently extended and simplified Voigt's classical theory, and Lande‡, by making use of inner quantum numbers and energy levels, has tried to explain some of the observed facts. Yet the new theory does not take us any further, and more research is required before any satisfactory explanation can be found for these anomalous results.

\* Zeeman, 'Magneto-optics,' p. 123.

† Sommerfeld, *Zeit. f. Physik*, viii. 257 (1922). Sommerfeld and Heisenberg, *Zeit. f. Physik*, xi. p. 131 (1923).

‡ Lande, *Zeit. f. Physik*, xi. p. 353 (1923).

LIX. *Some Notes on the Kinetic Theory of Viscosity, Conduction, and Diffusion.* By Prof. S. CHAPMAN and W. HAINSWORTH, B.Sc.\*

§ 1. *The Conduction of Energy and Momentum by Rotating Molecules.*

THE most satisfactory treatment of viscosity and thermal conduction which has yet been given, for gases composed of molecules which possess *rotatory* as well as *translatory* motion, is that due to Dr. F. B. Pidduck †. This was based on the molecular model suggested by Prof. G. H. Bryan ‡, namely a sphere which is rigid, elastic, and perfectly rough. The condition satisfied by the motions of two such molecules immediately after collision is that the relative velocity of separation, for the points instantaneously in contact, is equal and opposite to the velocity of approach of these points just before contact occurs. Such a model effectively promotes interchange between translatory and rotatory energy, while preserving the indispensable mathematical advantages attaching to the spherical symmetry of the molecule.

Perhaps the most interesting of Pidduck's results are those which concern the ratio  $f$ , defined by

$$f = \frac{\lambda}{\mu C_v}$$

where  $\lambda$  is the thermal conductivity,

$\mu$  is the viscosity,

$C_v$  is the specific heat at constant volume.

Theory and experiment agree in indicating that, for mono-atomic or non-rotating molecules,  $f$  is nearly equal to 2.5 §. Provided the molecule is spherically symmetrical and effectively smooth, so that it possesses no rotatory energy, the

\* Communicated by the Authors.

† Pidduck, F. B., Proc. Roy. Soc. (A), vol. ci. (1922).

‡ Bryan, G. H., Brit. Assoc. Report. p. 83 (1894).

§ Cf. Chapman, S., Phil. Trans. A, cccvi. pp. 279-348 (1915).

exact nature of the forces acting at encounters scarcely affects the value of  $f$ . For diatomic and polyatomic molecules, however,  $f$  is smaller and more variable: thus for hydrogen, nitrogen, and oxygen  $f$  is 1.90 or 1.91, for carbon monoxide and nitric oxide it is 1.88 and 1.86, for nitrous oxide it is 1.76, while for carbon dioxide and ethylene it is only 1.55\*.

Since viscosity represents a transference of momentum, and conduction a transference of energy, it is evident that the possession of rotatory energy diminishes the rate of transmission of molecular kinetic energy relative to that of momentum. The diminution is greater, moreover, the more the rotatory energy: in the above-named diatomic molecules the specific heats indicate that at ordinary temperatures the non-translatory energy corresponds to two degrees of freedom, the energy of any rotation which may occur about the axis of symmetry of the molecule being negligible, as the quantum theory would suggest; in the case of carbon-dioxide and ethylene, however, the non-translatory energy corresponds to more than two degrees of freedom, so that probably all three components of angular motion possess a share of the energy. Eucken† has shown that these values of  $f$  may be very fairly represented by the formula  $\frac{1}{2}(9\gamma-5)$ , where  $\gamma$  is the ratio of the specific heats; but this formula has no satisfactory theoretical foundation, and is moreover certainly too simple. Until Pidduck's paper appeared no numerically accurate calculations had been made for rotating molecules of a type even remotely comparable with actual molecules.

Pidduck found that with his model  $f$  is a function of the number  $K$ , where

$$K \equiv k^2/a^2,$$

$k$  being the radius of gyration and  $a$  the radius of the molecule. For a spherically symmetrical molecule  $K$  may range from 0 to  $2/3$ ‡, but  $f$  does not vary much with this change of  $K$ . For  $K=0$ ,  $1/5$ ,  $1/3$ , and  $2/3$  the values of  $f$  are (to a first approximation) 1.85, 1.87, 1.85, and 1.71.

\* (J. Jeans' 'Dynamical Theory of Gases,' 3rd edition, p. 284.

† Eucken, *Phys. Zeits.* xiv. p. 324 (1913).

‡ Presumably by oversight, Pidduck takes  $K$  as varying from 0 to 1, which extends the range of his results beyond what is mechanically possible;  $K=2/3$  corresponds, of course, to the case when all the mass is concentrated at the surface of the sphere.

These differ but little from the observed values of  $f$  for *diatomic* molecules, and the correspondence may be regarded as giving theoretical support to Eucken's view. Diatomic molecules seem likely, however, to be less well represented by a spherically symmetrical model than polyatomic molecules like those of  $\text{CO}_2$  or  $\text{C}_2\text{H}_4$ , for which Pidduck's values of  $f$  do not agree so closely with the observed values. It is therefore of interest to extend his work by taking a generalized form of his spherically symmetrical rotating model, embodying rather more accurately the properties of actual molecules. It is found that in this way the lower values of  $f$  may be accounted for, while the variation of  $\lambda$  and  $\mu$  with temperature is also more closely paralleled. It is mathematically scarcely practicable to take the non-sphericity of diatomic molecules into account in calculating  $f$ ; but Pidduck's results suggest that, as perhaps might be expected, the spheroidal form of such molecules enables them to transmute rotatory and translational energy into each other, during collisions, with the *maximum* efficiency which would be possible for any *spherical* molecule.

## § 2. *A Generalized Type of Rotating Molecule.*

The generalization of Pidduck's model which has been considered by us was suggested by the fact that, in the theory of a gas composed of *non-rotating* spherical molecules, any possible mode of interaction during collision may be treated mathematically as equivalent to elastic impact between rigid spheres, provided that the molecular diameter, instead of being taken as constant, is supposed to vary with the speed and directness of collision. The same idea may be applied to rotating molecules; the radius of gyration  $k$  is supposed invariable, the change in the distance of closest approach being supposed to occur in the region beyond that in which the mass (represented by the positive nuclei in actual molecules) is distributed; the collision-radius  $a$  is, however, regarded as variable, and as being expressed by

$$a = \sigma/x,$$

so that now

$$K = k^2/a^2 = (k^2/\sigma^2).x^2 \equiv K'.x^2, \quad . \quad . \quad . \quad (1)$$

where  $\sigma$  is a constant, and  $x$  is a variable which may be a function of any invariant of a molecular encounter, other



than the total momentum. In the present case  $x$  was taken to be a function of the component ( $V$ ) of the relative velocity of two colliding molecules, along the line of centres at impact. The function which was found most suitable for calculation is that which corresponds to the following formula for  $K$  (which by (1) is a multiple of  $x^2$ ):

$$K = \frac{2/3}{1 + \frac{b}{V^{2s}}}, \quad . . . . . (2)$$

where  $b$  and  $s$  are positive pure numbers characteristic of the type of molecule. If  $s > 0$ ,  $K$  increases with  $V$ , while the effective collision-radius ( $a$ ) diminishes. The maximum value of  $K$  allowed by the formula is  $2/3$ , in conformity with the condition of spherical symmetry; clearly  $K = 2/3$  when  $b = 0$  or  $V = \infty$ . When  $s = 0$ ,  $K$  and  $x$  are constant, so that this special case coincides with Pidduck's model, different values of  $K$  corresponding to different values of  $b$ . The development of the theory, using this model, is closely analogous to that in Pidduck's case, which itself was a direct extension of the theory for non-rotating molecules\*. The main difference in the final results is that certain integrals which occur in the expressions for  $\lambda$  and  $\mu$  are analytically reducible only when  $s = 0$  (Pidduck's case), so that in the general case they have to be evaluated by quadratures.

The formulæ actually obtained as first approximations to  $\lambda$  and  $\mu$  are as follows:

$$\lambda = \frac{3}{64K'\sigma^2} \left( \frac{R^3 T}{\pi m} \right)^{1/2} j_1(T),$$

$$\mu = \frac{15}{32K'\sigma^2} \left( \frac{mRT}{\pi} \right)^{1/2} j_2(T),$$

where  $T$  denotes the absolute temperature,  $m$  the molecular mass, and  $R$  the usual gas constant  $1.35 \times 10^{-16}$ , while

$$j_1(T) \equiv \frac{(I_3 + 3I_2)(12I_1 + 25I_2) - 3(4I_1I_3 - 25I_2^2)}{I_2(4I_1I_3 - 25I_2^2)}, \quad . \quad (3)$$

\* Chapman, S., Phil. Trans. A, ccxvi. (1915), or Enskog, D., Inaugural Dissertation, Upsala, 1917, and *Arkiv f. Mat., Astron. o Fysik, Stockholm*, xvi. (1921).

where

$$I_1 \equiv \int_0^\infty e^{-g} \left\{ \frac{13/4}{(1+K)^2} + \frac{g}{K(1+K)} \right\} dg,$$

$$I_2 \equiv \int_0^\infty e^{-g} \frac{dg}{(1+K)^2},$$

$$I_3 \equiv \int_0^\infty e^{-g} \left\{ \frac{2+g}{K(1+K)^2} + \frac{2(1+2g)+3K(1+g)}{(1+K)^2} \right\} dg,$$

and

$$f_2(T) \equiv \int_0^\infty e^{-g} \left\{ \frac{6Kg+6g+7K}{K(1+K)^2} \right\} dg. \quad . \quad . \quad . \quad . \quad (4)$$

$$g = \frac{1}{4} \frac{m}{RT} V^2.$$

In terms of  $g$ , (2) gives

$$K = \frac{2/3}{1 + b \left( \frac{m}{4RT} \right)^s g^{-s}};$$

so that the above integrals, and  $f_1(T)$ ,  $f_2(T)$ , are functions of  $T$  unless  $s=0$ .

For comparison with Pidduck's work, values of  $b \left( \frac{m}{4RT} \right)^s$  were determined for each of the values  $s=0.5$ ,  $s=0.7$ , and  $s=0.9$ \*, such that  $\bar{K}$  should equal  $1/5$ ,  $1/3$ , and  $2/3$ ,  $K$  being the mean of  $K$  averaged over all collisions. This leads to the formula :

$$K = \frac{2/3}{1 + \frac{(2j-3)T_0^s}{3T^s g^s \Gamma(1-s)}}, \quad . \quad . \quad . \quad . \quad (5)$$

where  $T_0$  is the temperature at which  $K$  is to have the above values, while  $j=5$ ,  $3$ , or  $3/2$  according as  $\bar{K}$  is equal to  $1/5$ ,  $1/3$ , or  $2/3$ .

The above formula, for the temperature  $T_0$ , gives the following values of  $f$  :—

$K$ .	$s=0$ .	$s=0.5$ .	$s=0.7$ .	$s=0.9$ .
0 .....	1.85	1.61	1.48	1.25
1/5 .....	1.87	1.66	1.50	1.29
1/3 .....	1.85	1.70	1.58	1.47
2/3 .....	1.71	1.71	1.71	1.71

\* The integrals involved in  $f_1(T)$  and  $f_2(T)$  do not converge if  $s>1$ .

The first column ( $s=0$ ) is a repetition of Pidduck's results. The values of  $f$  in the last row are constant because for  $\bar{K}$  to equal  $2/3$  it is necessary that  $b=0$ , and therefore the model again reduces to (a special case of) Pidduck's model. The remainder of the table is new, and indicates that as  $s$  increases, corresponding to increasing "softness" of the molecule, the value of  $f$  appreciably diminishes. The theoretical range of  $f$  is thus extended in the direction required to explain the observed values of  $f$  for such gases as carbon dioxide and ethylene. This is as far as one can expect to go in the direction of theoretical explanation at present, in view both of the intrinsic analytical difficulties of the statistical theory and our almost complete ignorance of the nature of molecular interaction during collisions.

### §3. *The Variation of Viscosity with the Temperature.*

The above generalization of Bryan's molecular model affords a better representation of the properties of actual gases in another respect, namely, in regard to the variation of viscosity and conductivity with temperature. Pidduck's results show that as long as the radius of the sphere is invariable (so that  $b=0$ , or  $s=0$ ),  $\lambda$  and  $\mu$  must be proportional to  $T^{1/2}$ , but our more general formulæ indicate that, when  $a$  varies with  $V$ ,  $\mu$  and  $\lambda$  also involve the factors  $f(T)$  which are functions of temperature (*cf.* (3), (4), (5)). Their analytical expression is highly complicated, but the functions themselves are of simple form. One or two examples have been worked out to illustrate this.

Two values of  $s$  and three values of  $b$  have been considered;  $b$  has been chosen so that  $K_0$ , the mean value, averaged over all collisions, of the square of the ratio of the radius of gyration to the collision-radius ( $k^2/a^2$ ) at the temperature  $0^\circ\text{C}$ ., shall have the values  $1/10$ ,  $1/5$ , or  $1/3$ . For higher temperatures the value of  $\bar{K}$  will be increased, because the radius of gyration, by hypothesis, remains constant, while with the greater molecular velocities the effective collision-radius will be decreased. The chosen values of  $s$  are  $0.5$  and  $0.9$ , the greater value corresponding to the "softer" molecule.

With these data, it is found that the viscosity  $\mu$  varies with absolute temperature  $T$  very approximately according to

the law  $T^n$ , over the range of temperature  $0^\circ \text{C.}$  to  $250^\circ \text{C.}$  (or  $273^\circ$  to  $523^\circ$  absolute). The values of  $n$  which give the best fit are given in the following table, which also illustrates the closeness of the fit, by including values of

$$\frac{\mu}{T^n} \bigg/ \frac{\mu_0}{T_0^n}$$

where the suffix 0 refers to  $0^\circ \text{C.}$  For  $T=273^\circ$  or  $0^\circ \text{C.}$  this expression is unity, while the table indicates that in other cases its value differs extremely little from unity.

Adopted data.		Values of $(\mu/T^n)/(\mu_0 T_0^n)$ for various temperatures.						Calculated.
$\bar{K}_0$ .	$s$ .	$0^\circ \text{C.}$	$50^\circ \text{C.}$	$100^\circ \text{C.}$	$150^\circ \text{C.}$	$200^\circ \text{C.}$	$250^\circ \text{C.}$	$n$ .
0.10	0.5	1.000	1.002	1.002	1.001	0.999	0.997	0.86
	0.9	„	1.004	1.005	1.004	1.000	0.997	0.80
0.20	0.5	„	0.993	0.997	1.001	1.001	1.001	0.75
	0.9	„	1.000	1.000	0.998	0.995	0.990	0.68
0.33	0.5	„	1.002	1.003	1.002	1.001	0.998	0.67
	0.9	„	1.005	1.000	1.000	0.995	0.995	0.60

The values of  $n$  given in this table clearly increase as  $\bar{K}$  diminishes and also as  $s$  diminishes. Since as  $s$  diminishes the molecule tends to Pidduck's case of the molecule of invariable size, it is at first sight surprising that  $n$  increases as  $s$  diminishes; but the reason for this is not improbably that, for such small initial values of  $\bar{K}$ , the softer the molecule (or the greater the value of  $s$ ) the more rapidly does  $\bar{K}$  tend, with increasing temperature, to the value  $2/3$ , another special case for which  $n=1/2$ .

The observed values of  $n$  exceed  $1/2$  for most known gases. For the diatomic gases hydrogen, oxygen, and nitrogen,  $n$  has the values 0.68, 0.74, and 0.78; while for carbon dioxide and ethylene it is 0.98 and 0.90. The above table does not quite cover this range of  $n$ , but indicates quite clearly that by taking  $\bar{K}_0$  still smaller than 0.1 larger values of  $n$  can be arrived at. Moreover, these smaller values of  $\bar{K}_0$  fit in well with the small observed values of  $f$  which correspond to gases like  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$ , for which the observed  $n$  is greatest. Thus the allowance for the "softness" of actual

molecules extends the theory of viscosity and conduction in gases whose molecules possess rotation, in the direction required in order to explain the observed facts.

#### § 4. *The Definition of Temperature.*

A further point to which attention may be drawn relates to the definition of the temperature  $T$  in the non-uniform state of the gas.

Let  $C$  denote the *peculiar* velocity of a molecule, *i.e.* its velocity relative to the mean motion at the point; then  $\frac{1}{2}mC^2$  is the translatory kinetic energy of a molecule relative to the mean motion. Let  $E$  denote the total kinetic energy of a molecule, namely,  $\frac{1}{2}mC^2$  together with any energy of rotation or oscillation which the molecule may possess. Let  $N$  denote the number of degrees of freedom of the molecule: for "monatomic" molecules  $N=3$ , for diatomic molecules  $N=5$ , while for the molecules considered in this paper  $N=6$ . If there is equipartition of energy between the various degrees of freedom,

$$\bar{E}/N = \frac{1}{2}m\bar{C}^2/3,$$

where the bar above  $E$  and  $C^2$  denotes that mean values are referred to. It is assumed in Pidduck's and the present work that this relation is satisfied in the steady state of the gas. It is not to be expected, however, that it will exactly hold good when the temperature or mean motion of the gas is not uniform. Hence the temperature of the gas will be reckoned differently according as one or other of the definitions

$$\frac{1}{2}NRT = \bar{E} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6 a)$$

or

$$\frac{3}{2}RT = \frac{1}{2}m\bar{C}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6 b)$$

is adopted. The latter is the one used by Jeans in his 'Dynamical Theory of Gases,' while Pidduck adopts the former; the two methods agree, of course, as applied to the steady state of the gas. Jeans's procedure seems preferable, however, because it preserves the validity of the important relation

$$p = nRT,$$

connecting the hydrostatic pressure  $p$  with the number density ( $n$ ) and the temperature of the gas; this follows from the fact that

$$p = \frac{1}{3}nm\bar{C}^2$$

whether the state of the gas is steady or unsteady.

The first approximation,  $F_0$ , to the velocity-distribution function,  $F$ , in the unsteady state is always taken to have Maxwell's form, which in the case of non-rotating molecules is

$$F_0 = n \left( \frac{m}{2\pi RT} \right)^{3/2} \exp \left( -\frac{E}{RT} \right),$$

where  $E$  is the molecular energy as defined above, and  $n$  is the number density. According as  $T$  is defined by (6a) or (6b), it will follow that the integral of either

$$(F - F_0)E \quad \text{or} \quad (F - F_0)\frac{1}{2}m\bar{C}^2$$

over all the molecules in any small volume must vanish. The latter relation implies that the *correct* hydrostatic pressure is obtained from the velocity-distribution function by using the first approximation; in the former case, however, this will not be so. This is not manifest in Pidduck's work, owing to the omission of a certain term in the additional expression ( $F_1$ ) which, with  $F_0$ , gives the second approximation to  $F$ . The second approximation to  $p$  derived from the corrected form of  $F$  is

$$p = nRT \left\{ 1 + \frac{1}{128\pi^{1/2}K'n\sigma^2I_2} \left( \frac{m}{RT} \right)^{1/2} \frac{D\rho}{Dt} \right\},$$

where  $\frac{D\rho}{Dt}$  is the rate of change of  $\rho$  in a small volume moving with the gas. The additional term in  $p$  is of small magnitude, but it seems better not to introduce it at all, as is assured by taking (6b) as the definition of temperature.

### § 5. The Coefficient of Diffusion.

It may be noted that the additional term in  $p$  does not vanish when  $K$  is equated to zero: this is not surprising when it is remembered that at the same time the angular velocity of the molecules must tend to infinity, if equipartition is to be maintained.

The first approximation to the coefficient of viscosity, however, reduces to the form appropriate to non-rotating molecules when  $K$  is equated to zero; and the same is true for the first approximation to the coefficient of diffusion ( $D_{12}$ ). The latter, which is not given by Pidduck, has been worked out, and may be quoted here:

$$D_{12} = \frac{3}{64\sigma_0^2 n_0 K_0' I_s} \left( \frac{2RTm_0}{m_1 m_2 \pi} \right)^{1/2},$$

where

$$m_0 = m_1 + m_2, \quad m_0 K_0 = m_1 K_1 + m_2 K_2,$$

$$\sigma_0 = \frac{1}{2}(\sigma_1 + \sigma_2), \quad n_0 = n_1 + n_2,$$

$$\frac{K_1}{K_1'} = \frac{K_2}{K_2'} = \frac{K_0}{K_0'} = x^2,$$

and

$$I_s = \int_0^\infty e^{-g} \left\{ \frac{K_1 K_2 (1+g) + K_0 g}{K_0 (K_0 + K_1 K_2)} \right\} dg.$$

For Pidduck's model this reduces to

$$D_{12} = \frac{3}{64\sigma_0^2 n_0} \left( \frac{2RTm_0}{m_1 m_2 \pi} \right)^{1/2} \frac{K_0 + K_1 K_2}{K_0 + 2K_1 K_2}.$$

### § 6. Thermal Diffusion: Non-rotating molecules.

The formula for the first approximation to  $D_T$ , the coefficient of thermal diffusion, in the case of non-rotating molecules, is

$$D_T = \frac{15n_1 n_2 RT}{4n_0^2 \Omega \Delta} \left\{ \frac{a_{10} a_{1-1} - a_{11} a_{0-1}}{n_1 m_2^{1/2}} + \frac{a_{1-1} a_{-10} - a_{10} a_{-1-1}}{n_2 m_1^{1/2}} \right\},$$

where

$$a_{10} = \frac{1}{2} \mu_2^2 m_1^{1/2},$$

$$a_{-10} = -\frac{1}{2} \mu_1^{3/2} (\mu_2 m_1)^{1/2},$$

$$a_{00} = (m_1 m_2 \mu_1 \mu_2)^{1/2},$$

$$a_{11} = \left\{ \sqrt{2\mu_2} \frac{\sigma_1^2}{\sigma_0^2} \frac{n_1}{n_2} + \mu_2 \left( \frac{5}{4} \mu_1^2 + 19\mu_1 \mu_2 + 12\mu_2^2 \right) - \frac{2}{2} \mu_1 - 15\mu_2 + \frac{25}{4} \right\},$$

$$a_{1-1} = a_{-11} = -\frac{2}{3} (\mu_1 \mu_2)^{3/2},$$

while  $a_{-1-1}$  is the same as  $a_{11}$  with the suffixes 1 and 2

interchanged. Also

$$\mu_1 = \frac{m_1}{m_0}, \quad \mu_2 = \frac{m_2}{m_0},$$

$$\Omega = 16 \left( \frac{2RT\pi}{m_0\mu_1\mu_2} \right)^{1/2} \sigma_0^2,$$

$$\Delta = \begin{vmatrix} a_{-1-1} & a_{-10} & a_{-11} \\ a_{0-1} & a_{00} & a_{01} \\ a_{1-1} & a_{10} & a_{11} \end{vmatrix}.$$

The second approximation to  $D_{12}$  is given by

$$D_{12} = \frac{3RT}{2n_0\Omega\Delta} (a_{-1-1}a_{11} - a_{1-1}^2).$$

These differ somewhat from the values formerly given by one of us\* ; the error, due to an oversight in algebra, was pointed out by Enskog†. The correction affects various numerical calculations which Chapman has given relating to thermal diffusion, but the error is fortunately of little importance. In the following special cases, these approximations to  $D_{12}$  and  $D_T$  and their ratio  $k_T$  take the forms :

(i.)  $\frac{m_1}{m_2} \longrightarrow \infty, \quad \sigma_1 = \sigma_2.$

$$D_{12} = \frac{3}{64n_0\sigma_0^2} \left( \frac{2RT}{m_2\pi} \right)^{1/2} \frac{4\sqrt{2n_2+13n_1}}{4\sqrt{2n_2+12n_1}},$$

$$D_T = \frac{15n_2}{256n_0^2\sigma_0^2} \left( \frac{2RT}{m_2\pi} \right)^{1/2} \frac{n_1}{\sqrt{2n_2+3n_1}},$$

$$k_T = 5 \frac{n_2}{n_0} \frac{n_1}{4\sqrt{2n_2+13n_1}}.$$

(ii.)  $\frac{m_1}{m_2} \longrightarrow \infty, \quad \frac{\sigma_1}{\sigma_2} \longrightarrow \infty.$

$$D_{12} = \frac{13}{256n_0\sigma_0^2} \left( \frac{2RT}{m_2\pi} \right)^{1/2},$$

$$D_T = \frac{5n_2}{256n_0^2\sigma_0^2} \left( \frac{2RT}{m_2\pi} \right)^{1/2},$$

$$k_T = \frac{5n_2}{13n_0}.$$

\* Chapman, Phil. Trans. A, ccxvii. pp. 166-185.

† *Arkiv f. Mat., Astron. o Fysik, Stockholm*, xvi. (1921).



The approximate value of  $k_T$  when  $n_1 = n_2$  is readily found to be 0.134 in case (i.) and 0.192 in case (ii.). It may be recalled that  $k_T$  is a measure of the difference of concentration of the gaseous constituents in two bulbs connected with one another by an open tube, but maintained at different temperatures\*.

The following tables, correcting those in the works already referred to, illustrate the order of magnitude of  $k_T$  in other less special cases:—

$$(iii.)\dagger \quad (a) \text{ Argon-Helium. } \frac{m_1}{m_2} = 9.8, \frac{\sigma_1}{\sigma_2} = 1.69.$$

$$k_T = \frac{5}{2n_0} \left\{ \frac{0.289n_1 + 0.210n_2}{2.165 + 1.895n_1/n_2 + 0.449n_2/n_1} \right\}.$$

$$(b) \text{ Oxygen-Hydrogen. } \frac{m_1}{m_2} = 16, \frac{\sigma_1}{\sigma_2} = 1.34.$$

$$k_T = \frac{5}{2n_0} \left\{ \frac{0.204n_1 + 0.177n_2}{1.630 + 1.320n_1/n_2 + 0.405n_2/n_1} \right\}.$$

$$(c) \text{ Oxygen-Nitrogen. } \frac{m_1}{m_2} = 16/14, \frac{\sigma_1}{\sigma_2} = 0.97.$$

$$k_T = \frac{5}{2n_0} \left\{ \frac{0.038n_1 + 0.041n_2}{3.689 + 1.777n_1/n_2 + 1.905n_2/n_1} \right\}.$$

The following table gives the numerical values of  $k_T$  for special cases of the above formulæ:—

$n_1/n_2$	$k_T$		
	(a).	(b).	(c).
1/3 .....	0.139	0.140	0.010
1 .....	0.138	0.142	0.013
3 .....	0.097	0.086	0.010

\* "A Note on Thermal Diffusion," Chapman and Dootson, Phil. Mag. xxxiii. p. 248 (March 1917).

† Phil. Trans. A, ccxvii. p. 185.

(iv.)\* (d) Carbon dioxide and hydrogen.  $\frac{m_1}{m_2}=22, \frac{\sigma_1}{\sigma_2}=\frac{1.64}{1.18}$ .

$$k_T = \frac{5}{2n_0} \left\{ \frac{0.183n_1 + 0.139n_2}{1.292 + 1.82n_1/n_2 + 0.292n_2/n_1} \right\}.$$

(e) Sulphur dioxide and hydrogen.  $\frac{m_1}{m_2}=32, \frac{\sigma_1}{\sigma_2}=\frac{2}{1.18}$ .

$$k_T = \frac{5}{2n_0} \left\{ \frac{0.182n_1 + 0.102n_2}{0.968 + 0.166n_2/n_1 + 1.201n_1/n_2} \right\}.$$

† The following table gives the calculated values of the percentage difference of composition for the gas in the two bulbs used in Dootson's experiments (*l. c.*), together with the values experimentally obtained. The reason for the discrepancy is that referred to in § 7.

Percent. difference of composition for the two bulbs.			
	No. of experiment.	Experimental value.	Calculated.
(d) .....	(1)	3.6	8.1
(d) .....	(2)	1.8	6.9
(d) ..	(3)	2.8	7.6
(e) ..	(5)	3.5	9.3

(v.) † (f) Ethylene and nitrogen.  $\frac{m_1}{m_2}=1, \frac{\sigma_1}{\sigma_2}=\frac{2.39}{1.84}$ .

$$k_T = \frac{5}{n_0} \left\{ \frac{0.068(n_1 - n_2) + 1.040n_0}{233.856 + 118(1.277n_1/n_2 + 0.757n_2/n_1)} \right\}.$$

The following numerical values of  $k_T$  are calculated from this formula.

$n_1/n_2$ .....	1/3.	1.	3.
$k_T$ .....	0.0091	0.0110	0.0075

§ 7. The above results refer to molecules typified by smooth elastic spheres of constant diameter:  $k_T$  is at its greatest for molecules of this type, while it vanishes altogether if the molecules are point centres of force varying inversely as

\* "A Note on Thermal Diffusion." p. 252.

† "The Partial Separation by Thermal Diffusion of Gases of Equal Molecular Weight," *Phil. Mag.* xxxiv. p. 146 (August 1917).

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the fifth power of the mutual distance  $r$ . The following table illustrates the approximate value of  $k_T$  for intermediate laws of force  $r^{-q}$ , and also indicates to what extent the first approximation to  $k_T$  is in error: this calculation is possible because by a method due to Lorentz an exact evaluation of  $k_T$  (and various other gaseous characteristics, including  $\lambda$  and  $\mu$ ) can be made when, as in case (i.), to which the present table refers,  $m_1/m_2 \rightarrow \infty$ ,  $\sigma_1/\sigma_2 \rightarrow \infty$ . The exact formula for  $k_T$  is found to be

$$k_T = \frac{n_2}{n_0} \frac{q-5}{2(q-1)},$$

while by the general method the first approximation to  $k_T$  for this case is given by

$$k_T = \frac{5n_2}{n_0} \left( \frac{q^2 - 6q + 5}{13q^2 - 42q + 45} \right).$$

$q$	$k_T$ (first approx.).	$k_T$ (exact).
5 .....	0	0
7 .....	0.155 $n_2/n_0$	0.167 $n_2/n_0$
9 .....	0.222 ..	0.250 ..
13 .....	0.283 ..	0.333 ..
17 .....	0.311 ..	0.375 ..
33 .....	0.350 ..	0.438 ..
$\infty$ .....	0.385 ..	0.500 ..

It is clear that the error of the first approximation increases and becomes quite considerable as the case  $q = \infty$ , corresponding to molecules which behave like rigid elastic spheres, is approached.

(*g*) The most accurate experiments on thermal diffusion which have yet been made are those by Mr. T. L. Ibb\*.

In an appendix to Ibb's paper, Chapman compared certain of Ibb's results with the theoretical formula. These results gave the *difference* of concentration of the two gases carbon dioxide and hydrogen in connected bulbs maintained at different temperatures, as a function of the mean relative proportion of the two gases. The corrected theoretical formula for this mixture has been given above, and the

\* "Some Experiments on Thermal Diffusion," Proc. Roy. Soc. ser. A. xcix. no. A. 700, p. 385.

values of  $k_T$  for various mean relative concentrations of the two gases are :

Percent. $\text{SO}_2$ .	Percent. $\text{H}_2$ .	$k_T$ calculated.
10	90	0.105
20	80	0.152
30	70	0.168
40	60	0.166
50	50	0.152
60	40	0.130
70	30	0.103
80	20	0.071
90	10	0.037

These figures do not differ much from those previously given, but it is satisfactory to find that the revision brings the values into even closer agreement than before with Ibb's observed data.

#### *Summary.*

(a) Pidduck's theory of viscosity and thermal conduction in polyatomic gases (*i.e.* gases possessed of rotatory as well as translatory energy) is generalized with the aid of a molecular model which takes account of the varying distance of closest approach between molecules depending on their relative speed of impact. The calculated values of the ratio  $f$  (§ 1), and of the variation of viscosity with temperature (§ 3), are thus brought into closer agreement with the observed results for various diatomic and polyatomic gases.

(b) The definition of temperature in the non-steady state of a polyatomic gas is discussed (§ 4), and it is pointed out that the definition used by Jeans is preferable to that used by Pidduck, since it avoids the introduction of an additional term in the usual expression for the hydrostatic pressure.

(c) A formula for the coefficient of diffusion appropriate to a polyatomic gas is given (§ 5).

(d) Revised formulæ and tables for various quantities connected with thermal diffusion in a monatomic gas are given (§§ 6, 7) correcting values previously published.

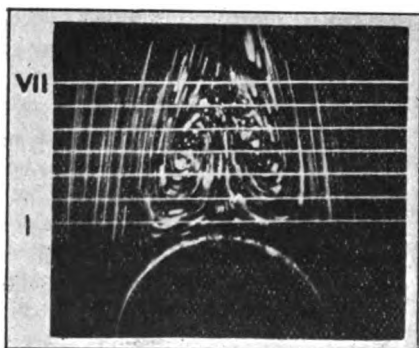
LX. *Eddies in Air.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,--

I SHALL be glad if you will publish the following corrections to the paper on Eddies in Air (vol. xlvi. Nov. 1923, p. 754).

The name of my colleague was Hisamitu Nisi, and not as given inadvertently at the head of the paper.



The actual figure from which the measurements in the case of the cylinder were made is given herewith; the one shown as fig. 11, though also for a cylinder, was not the one utilised.

Yours faithfully,  
ALFRED W. PORTER.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[SIXTH SERIES.]

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OCTOBER 1924.

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LXI. *On the Passage of Light Through Transparent Plates.*  
By Sir ARTHUR SCHUSTER, D.Sc., F.R.S.\*

[Plate XII.]

IN explaining the optical effects observed under suitable conditions in light that has passed through transparent plates, it is the present practice to select certain groups of rays and to apply the principle of interference. I propose to substitute a more rational procedure which discards the conception of rays and seeks guidance by following the wave-fronts. It is my object to show that this method is more general and more effective. As an illustration I take the so-called interference effects observed in parallel light after its passage through two mutually-inclined transparent plates, Brewster's bands being a special case of the general problem. Owing to the inclination of the plates, backward and forward reflexions *between* the plates need not be taken into account.

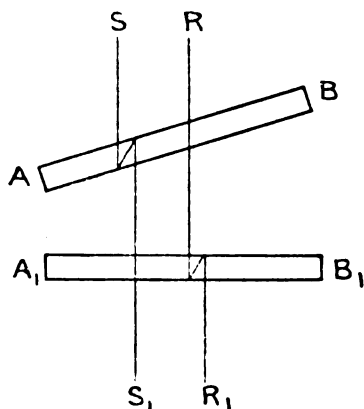
The current method is to select two rays  $RR_1$  and  $SS_1$  (fig. 1) of which the former has passed through the first plate (AB) and been twice internally reflected in the second ( $A_1B_1$ ), while the latter has suffered two internal reflexions

\* Communicated by the Author.

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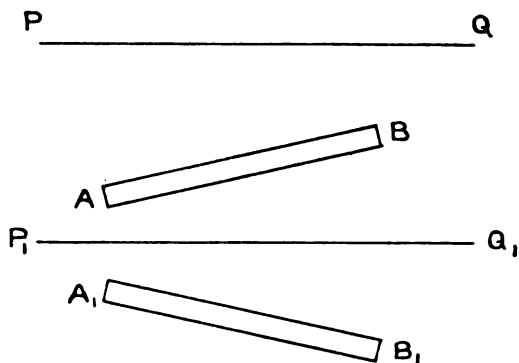
in  $AB$  and passed straight through  $A_1B_1$ . A slight difference in path due to an inclination of one of the plates or a difference in thickness will cause a change of the combined amplitudes by so-called interference. The complete solution requires a lengthy calculation, rays that have been internally reflected more than twice being taken into account.

Fig. 1.



If, on the contrary, we consider not rays but wave-fronts, the problem presents an altogether different and simpler aspect. The wave-front  $PPQ$  (fig. 2) having passed

Fig. 2.



through  $AB$  and reached a position such as  $P_1Q_1$ , is no further concerned with  $AB$ . Its subsequent fate depends entirely on the second plate. If  $J_1$  represents the fraction of the intensity of light that passes through  $AB$  and  $J_2$  the

corresponding fraction for  $A_1B_1$ , the intensity transmitted through the combined plates is simply  $J_1J_2$ . There is here no question of interference: we do not add amplitudes, but multiply transmittances.

I shall assume the effects of a single plate to be known. To an eye focussed for infinity, homogeneous light appears as a succession of bright and dark rings, and the greater the reflecting power of the plate, the more will the light be concentrated in the circles of maximum intensity until, in the limit, when the reflecting power is equal to unity, the bright rings are reduced to lines. With two plates, acting independently, each would produce a system of concentric rings. In Pl. XII. the two systems are drawn with P and Q as centres, and the combined effect is obtained by taking the product of the separate intensities. It is apparent that the maxima will be concentrated at the intersection of the circles, and in the limiting case of linear rings the light is entirely confined to a number of points, the position of which is easily calculated. If the centre of each system is a point of maximum intensity, the radii of rings having maximum intensity are in the ratio of the square roots of successive integer numbers. Referred to a system of coordinates in which the line joining the two centres is the axis of  $x$  and the origin is at a point half-way between the centres, the rings are represented by the equations

$$y^2 + (x-a)^2 = R^2m; \quad y^2 + (x+a)^2 = R^2n,$$

where  $m$  and  $n$  are integers and  $R$  is a linear constant. Subtracting and adding these equations, we find

$$4ax = R^2(n-m); \quad y^2 + x^2 = \frac{1}{2}R^2(m+n).$$

Hence the points of maximum intensity for equal values of  $m-n$  lie on equidistant straight lines parallel to the axis of  $y$  and, for equal values of  $m+n$ , on circles having the origin of coordinates (O) as centre. Pl. XII. shows the lines of maximum intensity in the original system of rings as well as the straight lines and circles having O as centre.

For a complete solution of the distribution of intensities, we must turn to Airy's equation for a single plane parallel plate. To an eye focussed for infinity the intensities are represented by

$$J = \frac{(1-s)^2}{(1+s^2) - 2/s \cos \delta},$$

2 T 2



where  $s$  is the coefficient of reflexion at the surface of the plate, and the angle  $\delta$  is defined by

$$\delta = 4\pi e \cos \gamma / \lambda,$$

$\gamma$  denoting the angle between the wave normal and the plate normal inside the plate, and  $\lambda$  the wave-length, also measured inside the plate, while  $e$  is its thickness. For a combination of two plates we have therefore

$$I = J_1 J_2 = \frac{(1-s_1)^2}{(1+s_1^2) - 2s_1 \cos \delta_1} \cdot \frac{(1-s_2)^2}{(1+s_2^2) - 2s_2 \cos \delta_2} \quad (1)$$

In the problems which are of practical importance we may assume  $s_1$  and  $s_2$  to have the same value. It is convenient to substitute for  $\delta_1$  and  $\delta_2$  two other variables  $\epsilon$  and  $\zeta$ , such that

$$2\epsilon = \delta_1 + \delta_2; \quad 2\zeta = \delta_1 - \delta_2.$$

Writing

$$I = (1-s)^4 / D,$$

we then find:

$$D = (1-s^2)^2 + 4s^2(\cos^2 \epsilon + \cos^2 \zeta) - 4s(1+s^2) \cos \epsilon \cos \zeta, \quad (2)$$

or if

$$a = 1 + s^2; \quad b = 2s,$$

$$D = (a^2 - b^2) \sin^2 \zeta + (b \cos \epsilon - a \cos \zeta)^2. \quad (3)$$

These equations are perfectly general, but in what follows we shall confine ourselves to two plates of equal thickness.

Let the normals to the two plates be in the plane of  $xy$  and form equal angles  $\pm \alpha$  with the axis of  $x$ . The observing eye E (fig. 3) being in the axis of  $x$ , we take a line of sight ES forming an angle  $\phi$  with the axis of  $x$  so that the direction cosines of the line of sight are

$$\cos \theta \cos \phi, \quad \cos \theta \sin \phi, \quad \sin \theta.$$

If the angles between the two mirrors be  $2\alpha$ , the line of sight will form angles  $\gamma_1$  and  $\gamma_2$  with the normals to the plates, which are determined by

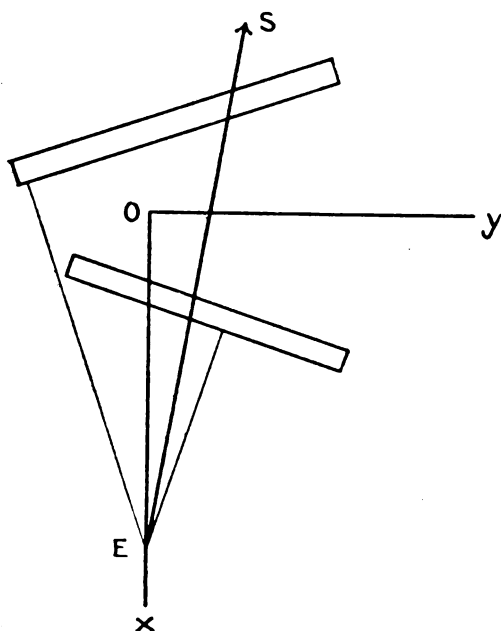
$$\cos \gamma_1 = \cos \theta \cos (\phi - \alpha); \quad \cos \gamma_2 = \cos \theta \cos (\phi + \alpha).$$

If  $p$  be the distance of E from the origin, the point at which the line of sight cuts the plane  $yz$  is

$$x = p = r \cos \theta \cos \phi, \quad y = r \cos \theta \sin \phi, \quad z = r \sin \theta,$$

the value of  $r$  for a given line of sight being determined by the first of these equations.

Fig. 3.



In order to avoid unessential complications, we take the optical medium to be air, as in Fabry and Perot's interferometer, so that the direction of the line of sight is not altered by its entry into the plates. Writing  $c$  for  $e/\lambda$ , we then have

$$\left. \begin{aligned} \delta_1 - \delta_2 &= 2\pi c(\cos \gamma_1 - \cos \gamma_2) = 4\pi c y \sin \alpha / r \\ (\delta_1 + \delta_2) &= 2\pi c(\cos \gamma_1 + \cos \gamma_2) = 4\pi c p \cos \alpha / r \end{aligned} \right\} \dots (4)$$

The second of these equations shows that lines drawn in the directions for which  $\delta_1 + \delta_2$  has the same value cut the plane  $yz$  in circles, the radii ( $R$ ) of which are determined by the equation after substitution of  $p^2 + R^2$  for  $r^2$ . If the line of vision be—as will usually be the case—confined to directions forming small angles with the axis of  $x$ , we may in the first equation take approximately  $r$  to be equal to  $p$ . The locus of the lines in the plane  $yz$  for which  $\delta_1 - \delta_2$  is constant are straight lines, two successive lines at which  $\delta_1 - \delta_2$  differs by  $2\pi$  being separated by a distance  $p/2c \sin \alpha$ . Without approximation, and referred to a system of coordinates parallel to the one used above, but passing through the point of observation  $E$  (fig. 3), the directions for which  $(\delta_1 - \delta_2)$

has constant value lie on the cone

$$(1 - \kappa_1^2)y^2 - \kappa_1^2(x^2 + z^2) = 0, \quad . \quad . \quad . \quad (5)$$

while the directions for which  $\delta_1 + \delta_2$  is constant lie on the circular cone

$$(\kappa_2^2 - 1)x^2 + \kappa_2^2(y^2 + z^2) = 0, \quad . \quad . \quad . \quad (6)$$

where

$$\kappa_1 = (\delta_1 - \delta_2)/4\pi c \sin \alpha; \quad \kappa_2 = (\delta_1 + \delta_2)/4\pi c \cos \alpha,$$

$\kappa_1$  and  $\kappa_2$  are fractions, being respectively equal to  $y/r$  and  $p/r$ , so that  $\kappa_1$  is small and  $\kappa_2$  is nearly equal to unity. The first of these cones cuts the plane  $x = p$  in a curve, the equation of which is

$$(1 - \kappa_1^2)y^2 - \kappa_1^2z^2 = \kappa_1^2p^2.$$

This represents an hyperbola. If  $z$  be small compared with  $p$ , the equation reduces to that of the straight lines

$$y = \kappa_1 p = (\delta_1 - \delta_2)p/4\pi c \sin \alpha,$$

in agreement with what has been found above.

The cones which define the directions for which  $\delta_1 - \delta_2$  and  $\delta_1 + \delta_2$  have constant values are fixed in space for a given position of the optical plates. The equations may therefore be modified, and applied to any directions of vision by determining the intersections of the cones with planes which are at right angles to the required line of vision, or preferably refer the cones to a system of coordinates in which the plane  $yz$  is normal to that line.

It is not my object to discuss particular cases, but two obvious conclusions may be mentioned. The lines for which  $\delta_1 - \delta_2$  is constant are determined by the cone defined by equation (5), which represents a surface of revolution round the axis  $y$ . Revolving this cone round its axis leaves it unchanged, and hence, so long as the point of observation remains in the plane  $xz$ , the locus of  $\delta_1 - \delta_2$  remains the same. That plane is fixed relatively to the plates. On the other hand, the locus for  $\delta_1 + \delta_2$  is a cone of revolution having the axis of  $z$  as axis, and we may therefore turn the mirrors round that axis without changing the curves for which  $\delta_1 + \delta_2$  has a constant value.

The circles and straight lines shown in Pl. XII. all pass through the points of maximum intensity, but within each line the intensity fluctuates. It is of interest to calculate the average intensity for the loci of constant  $\delta_1 - \delta_2$ . Equation (1) shows that there is a maximum of intensity when  $\cos \delta_1 = \cos \delta_2 = 1$ , and a minimum when  $\cos \delta_1 = \cos \delta_2 = -1$ .

If  $\zeta = 2m\pi$ , we find by the definition of  $\zeta$  and  $\epsilon$  that of  $\cos \delta_1 = \cos \delta_2$ . The lines so defined contain, therefore, both the maxima and the minima according as  $\cos \epsilon = \pm 1$ . Substituting this value of  $\zeta$  in equation (3), we find for the corresponding average intensity

$$\frac{1}{\pi} \int_0^\pi \frac{(1-s^4)d\epsilon}{[2s \cos \epsilon - (1+s^2)]^2} = \frac{(1-s)(1+s^2)}{(1+s)^3} \quad (7)$$

Along intermediate lines for which  $\sin \zeta = 1$  the intensity never rises so high or falls so low. The average intensity is in this case determined by

$$\frac{1}{\pi} \int_0^\pi \frac{(1-s^4)d\epsilon}{(1-s^2)^2 + 4s^2 \cos \epsilon} = \frac{(1-s)^3}{(1+s)(1+s^2)} \quad (8)$$

Before drawing any conclusions from these equations, we shall express equation (1) in the form of a series which will occasionally be found convenient when approximate results are sufficient and more especially when  $s$  is small.

For  $s_1 = s_2$  we may write (1) in the form

$$I = J_1 J_2 = \frac{(1-s)^2 (J_2 - J_1)}{2s(\cos \delta_2 - \cos \delta_1)}$$

and apply the equation

$$\frac{1-s^2}{1-2s \cos \delta + s^2} = 1 + 2(s \cos \delta + s^2 \cos 2\delta + s^3 \cos 3\delta \dots), \quad (9)$$

which can be verified by adding the series on the right-hand side. Writing  $S_1$  or  $S_2$  for the series according as it contains  $\delta_1$  or  $\delta_2$ , we have

$$J_1 = \frac{(1-s)^2}{1-s^2} S_1; \quad J_2 = \frac{(1-s)^2}{1-s^2} S_2$$

and

$$J_2 - J_1 = \frac{1-s}{1+s} (S_2 - S_1),$$

from which we obtain

$$I = \frac{(1-s)^3}{1+s} \frac{S_2 - S_1}{2s(\cos \delta_2 - \cos \delta_1)}.$$

With the previous definition of  $\zeta$  and  $\epsilon$ , and writing

$$P_m = \frac{\sin m\zeta}{\sin \zeta}, \quad Q_m = \frac{\sin m\epsilon}{\sin \epsilon},$$

we find

$$I = \frac{(1-s)^3}{1+s} [1 + sP_2Q_2 + s^2P_3(Q_3 + \dots)].$$

Applying the equation

$$\sin(m+1)\theta - \sin(m-1)\theta = 2 \sin \theta \cos m\theta,$$

we easily find for odd values of  $m$

$$Q_m = 1 + 2[\cos 2\epsilon + \cos 4\epsilon + \dots + \cos(m-1)\epsilon],$$

and for even values of  $m$

$$Q_m = 2[\cos \epsilon + \cos 3\epsilon + \dots + \cos(m-1)\epsilon] \dots$$

The series for  $P_m$  is obtained by substituting  $\zeta$  for  $\epsilon$ . We shall use these equations for the calculation of the average intensity along a line of constant  $\zeta$ . Noting in the first place that the average of  $Q_m$  is zero whenever  $m$  is even and equal to unity when  $m$  is odd, we may write down the average intensity at once as being

$$I = \frac{(1-s)^3}{s(1+s)} [s + s^3 \cos 3\zeta + s^5 \cos 5\zeta + \dots].$$

The series can be added up, and we finally have, writing  $[I(\zeta)]$  for the average intensity, along the lines for which  $\delta_1 - \delta_2$  is constant

$$[I(\zeta)] = \frac{(1-s)^3}{1+s} \cdot \frac{1+s^2}{1+s^4-2s^2 \cos 2\zeta} \dots \quad (9)$$

The maximum average is obtained when  $\zeta$  is a multiple of  $\pi$ , and the minimum when  $\zeta$  is an odd multiple of  $\frac{\pi}{2}$ .

In these two special cases we have already obtained the result by direct integration (see equations (7) and (8)). The ratio of the minimum to the maximum average intensities is

$$[(1-s^2)/(1+s^2)]^2.$$

Equation (3) shows that  $\epsilon$  and  $\zeta$  are interchangeable, so that we have along the lines for which  $\delta_1 + \delta_2$  is constant

$$[I(\epsilon)] = \frac{(1-s)^3}{1+s} \cdot \frac{(1+s^2)}{1+s^4-2s^2 \cos 2\epsilon}.$$

The intensities along the circles at which  $\delta_2$  is constant are given by (1), and we find the average intensity either by integration or by making use of the series in (9):

$$[I(\delta_2)] = \frac{(1-s)^3}{(1+s)(1+s^2-2s \cos \delta_1)},$$

which has a maximum value of  $(1-s)/(1+s)$  and a minimum

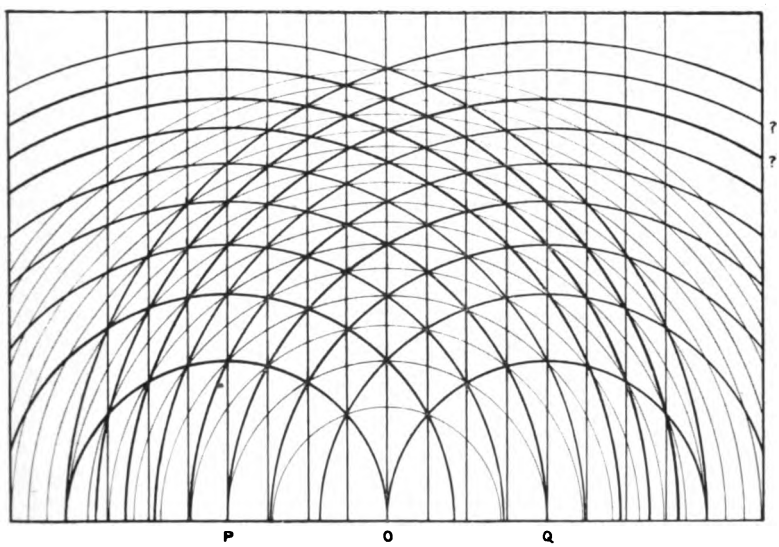
value of  $(1-s)^3/(1+s)^3$ , the ratio of the minimum to the maximum being  $(1-s)^2/(1+s)^2$ .

I have entered at some length into the question of these average intensities in order to form some judgment as to the interpretation which ocular vision would give to these overlapping circles and lines. A photograph was kindly taken for me by Mr. Twyman with two Fabry and Perot plates of equal thickness and slightly inclined to each other. Most prominent in the picture are the sets of overlapping circles which coincide with the circles due to each plate separately. The circles having O (see Pl. XII.) as centre, along which  $\delta_1 + \delta_2$  is constant, are not visible at all, and the straight lines for which  $\delta_1 - \delta_2$  has constant value are well shown in some of the outlying parts of the field. The photographs are not, however, as clear as could be wished, and show signs that the illumination was not uniform.

Mascart, in his 'Optics,' vol. i. p. 455, gives a picture of two sets of circles crossed by strongly-marked straight lines, without any sign of the set of circles for which  $\delta_1 + \delta_2$  is constant. The optical arrangement which gave this pattern is not very clearly described, but so far as I can understand its essential part approximates to that obtained from two plates, one of which acts by reflexion and the other by transmission. Some allowance should be made in a drawing for the probable omission of the less striking parts of the picture. We may conclude, however, that the circles of constant  $\epsilon$  do not strike the eye as those of constant  $\zeta$  or  $\delta$ . Some explanation is necessary to account for this. It will be remembered, of course, that each line of maximum average intensity is subject to fluctuations, the amount of which may be judged by an inspection of the accompanying table. This gives for four values of the reflecting power of  $s$  and different values of  $(\delta_1 + \delta_2)$  the calculated intensities, when  $\delta_1 - \delta_2$  is equal to zero or a right angle. These are the two values of  $\zeta$  for which the intensity is respectively greatest and least. The average intensities are given at the bottom of the table, and the numbers in square brackets indicate the ratio of these averages. As  $\zeta$  and  $\epsilon$  are interchangeable, there is no reason here why the circles ( $\zeta = \text{constant}$ ) should be less prominent than the straight lines at which  $\epsilon$  is constant. In the lowest row I have entered the average intensities and their ratio for the circles at which  $\cos \delta$  is either plus or minus unity. It is seen that there is along these lines a greater contrast between the circles of maximum and minimum light which may account for their greater

TABLE.

$\epsilon$ .	$s=2$ .		$s=4$ .		$s=6$ .		$s=8$ .	
	$\zeta=0$ .	$\zeta=90^\circ$ .	$\zeta=0$ .	$\zeta=90^\circ$ .	$\zeta=0$ .	$\zeta=90^\circ$ .	$\zeta=0$ .	$\zeta=90^\circ$ .
$0^\circ$ .....	1.000	.379	1.000	.096	1.000	.014	1.000	.001
15 .....	.959	.382	.864	.100	.634	.015	.180	.001
30 .....	.852	.393	.594	.109	.249	.017	.025	.001
45 .....	.714	.409	.367	.126	.098	.023	.006	.001
60 .....	.580	.417	.224	.150	.044	.033	.002	.002
75 .....	.467	.410	.143	.173	.023	.050	.001	.005
90 .....	.379	.444	.096	.184	.014	.062	.001	.012
105 .....	.314	.440	.069	.173	.009	.050	.000	.005
120 .....	.266	.417	.053	.150	.007	.033	.000	.012
135 .....	.234	.409	.044	.126	.005	.023	.000	.001
150 .....	.213	.393	.038	.109	.004	.017	.000	.001
165 .....	.202	.382	.035	.100	.004	.015	.000	.001
180 .....	.198	.379	.034	.096	.004	.014	.000	.001
Averages $\zeta$ ...	.481 [853]	.410	.254 [523]	.133	.133 [221]	.029	.050 [448]	.003
Averages $\delta$ ...	.667 [444]	.596	.429 [184]	.079	.250 [062]	.016	.111 [012]	.001







visible prominence. We have, further, to remember that the distances from maximum to minimum, as measured by the angular differences of the variables, do not correspond to equal linear distances in the pattern. It will be noted, *e. g.*, that the first circles with P and Q as centres will, when completed below the central line PQ, have 14 maxima, while the second circle having O as centre, which has the same diameter, has only 8 such maxima. This is probably the reason that in the grouping of the visible maxima of light the eye prefers to follow the lines along which the maxima are closer together. Further experiments with more perfect adjustment seem to be desirable.

In this communication only one of the several variations of the problem has been discussed in considerable detail, but there will be no difficulty in extending the investigation to light reflected from the plates instead of being transmitted. I may have another opportunity of treating the case where the two plates have not the same thickness, or when a small difference of thickness is partly compensated by a third plate.

August 11th, 1924.

*Note.*—I cannot help remembering that this is the fiftieth anniversary of the publication of the first of my papers that have from time to time appeared in the Philosophical Magazine.

A. S.

LXII. *Second Memoir on the Determination of the Curvature Invariant of Space-Time.* By L. SILBERSTEIN, Ph.D.\*

IN my first paper on this subject (Phil. Mag. for May, pp. 907–918) the case of radial inertial motion in de Sitter's space-time was considered. The rigorous spectrum-shift formula there deduced was

$$D \equiv \frac{\delta\lambda}{\lambda} = \gamma[1 \pm \sqrt{1 - \cos^2 \sigma / \gamma^2}] - 1, \dots (1)$$

with  $\gamma$  written for the integration constant

$$\gamma = \cos^2 \sigma \cdot c \, dt/ds \, \dagger. \dots (2)$$

Having unnecessarily limited myself to stars passing, in the

\* Communicated by the Author.

† In the first paper, p. 910, line 11,  $\cos \sigma$  is a misprint for  $\cos^2 \sigma$ .

future or the past, through the Sun as observing station with a velocity  $v_0 = c\beta$ , I wrote for this constant  $(1 - \beta^2)^{-\frac{1}{2}}$  and considered it, therefore, as essentially greater than unity. Thus the working formula, for small  $\sigma$  and  $\beta$ , became

$$D^2 = \sigma^2 + \beta^2, \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

with  $\beta^2 > 0$ , giving rise to incidental remarks to the effect that  $|D| \geq r/R$  or that, if the world-radius  $R$  be determined from a distant celestial object, neglecting its  $\beta$ , the value of  $R$  is underestimated. Thus also, if a single remote object were to show a rather small or a vanishing Doppler effect, it would rule out the  $R$ -value based on no matter how numerous other objects.

Now, Mr. P. Du Val in a recent private letter has drawn my attention to the possibility of  $\gamma < 1$ , corresponding, that is, to radial orbits *not* passing through the Sun, and I feel the more grateful, as his remark has enabled me to remove once for all the aforesaid difficulty or prospective danger.

In fact, by (2), and since  $ds^2 = \cos^2 \sigma \cdot c^2 dt^2 - dr^2$ ,

$$\gamma = \frac{\cos^2 \sigma}{\sqrt{\cos^2 \sigma - r^2/c^2}}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $r = |dr/dt|$ . Thus, if the star's orbit does pass through the Sun,  $\gamma = (1 - \beta^2)^{-\frac{1}{2}}$ , as before. But if it does not, and if at its "perihelion"

$$r = r_m = R\sigma_m,$$

we have, owing to  $v_m = 0$ ,

$$\gamma = \cos \sigma_m.$$

If this be introduced into (1), the approximate formula for small  $\sigma_m$  becomes

$$D^2 = \sigma^2 - \sigma_m^2 = \frac{r^2 - r_m^2}{R^2}, \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

as an alternative to (1a). Thus for any object  $|D|$  may be either greater or smaller than  $r/R$ , without contradicting the  $R$ -value based on other material. Nay, we can have  $D=0$  even for a very distant star or cluster, if it just happens to pass through its perihelion or, practically, if  $r - r_m$  does not exceed a hundred light-years or so. As long as we confine our attention to radial motions, both cases, with the corresponding formulæ (1a) or (1b), appear equally likely. Consequently, in a correlation table, with  $|D|$  as ordinates plotted against  $r$  as abscissæ, the

representative points, while showing a tendency to crowd near a straight line  $|D| = r/R$  drawn through the origin, may be scattered *both above and below this line*, without invalidating the adopted  $R$ -value.

Such a correlation table, based upon all the existing data for objects not nearer than several thousand parsecs, will be given and discussed in the sequel.

Our next task, however, is to give up even the limitation to radial motions. In fact, such motions of stars, although very convenient to the mathematician, as they require him to deal only with two dimensions  $(r, t)$ , are extremely unlikely to cover any actual case of a celestial object. Not one in many thousand of such objects can be reasonably expected to move just away or just towards the Sun, or even only the region of the solar system. And, although the transversal component of motion will give only a non-observable second-order effect, yet the radial velocity component  $v_r$  (which is practically responsible for the whole effect) may, for oblique motion, be a more complicated function of distance than for purely radial motion.

Let us, therefore, consider the general case of any, oblique, inertial motion of a star  $S$  relatively to the Sun, with any perihelion distance  $r_m = R\sigma_m$ .

As is well known, any such orbit is plane, though not a straight line of the elliptic space. It will be convenient to place the origin of coordinates,  $r, \theta$ , at  $S$ , as the sending station of light signals. Then the proper time  $s'$  of the star will be identical with the system-time, while that of the observer, reduced to the Sun, will be given by

$$ds^2 = \cos^2 \sigma \cdot c^2 dt^2 - dr^2 - R^2 \sin^2 \sigma \cdot d\theta^2, \quad \dots \quad (4)$$

and the Doppler effect will be determined by

$$D = \frac{ds}{ds'} - 1, \quad \dots \dots \dots (5)$$

as explained in the first paper. The equations of the observer's world-geodesic, or of free motion, are

$$\frac{R}{c} \frac{d\sigma}{dt} = \pm \cos \sigma \sqrt{1 - \frac{\cos^2 \sigma}{\gamma^2} - \frac{p^2 \cot^2 \sigma}{R^2 \gamma^2}} = \pm \frac{v_r}{c}, \quad (6a)$$

$$\frac{d\theta}{dt} = \frac{cp}{\gamma R^2 \cot^2 \sigma}, \quad \dots \dots \dots (6b)$$

where  $\gamma, p$  are integration constants,

$$\gamma = \cos^2 \sigma \cdot c dt/ds, \quad p = R^2 \sin^2 \sigma \cdot d\theta/ds. \quad \dots \quad (6c).$$

We may notice that the corresponding orbit may be written

$$\sin^2 \sigma \left[ 1 + \frac{2 - A \cos 2\theta}{A \cos 2\theta_p} \right] = \frac{2}{A},$$

where  $A = 1 + (\gamma^2 - 1)R^2/p^2$ , the angle  $\theta$  being counted from the axis of symmetry or the perihelion, and  $\pm \theta$  being its value where the orbit, resembling an hyperbola, meets the star's polar. But this integrated form of the orbit will not be needed for the purpose in hand, which is the evaluation of  $ds$  corresponding to  $ds'$ .

The light rays issuing from the star as origin are simply the straight radii vectores  $\theta = \text{const.}$  The wave fronts are spheres,  $r = \text{const.}$ , centred at  $S$ . Thus, let such a wave start from  $S$  at  $t = \alpha$ , and another at  $t = \alpha + d\alpha$ .

The first of these waves will reach the observer at  $P_1(r, \theta)$  at an instant  $t_1$ , and the second at  $P_2(r + dr, \theta + d\theta)$  at  $t_2 = t_1 + dt$ . The star's proper time elapsing between the two signals being  $ds' = c d\alpha$ , we require  $ds$ , the observer's proper time elapsing between the receiving of the first and the second signal. Now, by the first of (6c), the element (4) can be written

$$ds^2 = \frac{R^2(d\sigma^2 + \sin^2 \sigma d\theta^2) \cos^2 \sigma}{\gamma^2 - \cos^2 \sigma} \quad \dots \quad (7)$$

It remains to express  $d\sigma, d\theta$  in terms of  $d\alpha = ds'/c$ .

The propagation of light from  $S$  being ruled by  $\cos \sigma \cdot c dt = R d\sigma$ , we have

$$c(t_1 - \alpha) = \int_0^\sigma R \sec \sigma d\sigma, \quad c(t_2 - \alpha - d\alpha) = \int_0^{\sigma + d\sigma} idem,$$

whence  $c(dt - d\alpha) = R \sec \sigma d\sigma$ , i. e.,

$$c dt = ds' + R \sec \sigma d\sigma.$$

Eliminate  $dt$  by using (6a), thus finding  $d\sigma$  in terms of  $ds'$ . Next find  $d\theta/d\sigma$  by dividing (6a) by (6b), and substitute  $d\sigma, d\theta$  thus determined into (7). Then, after some very simple reductions, the result will be

$$\frac{ds}{ds'} = \frac{\cos^2 \sigma}{\gamma} : \left[ 1 \mp \sqrt{1 - \frac{\cos^2 \sigma}{\gamma^2} \left( 1 + R^2 \frac{p^2}{\sin^2 \sigma} \right)} \right],$$

which is the required ratio of the proper times. The signs - and + correspond to receding and to approaching motion respectively, and  $r = R\sigma$  is the distance of the

observer from the star at the instant of taking its spectrogram \*.

Ultimately, therefore, by formula (5), the rigorous value of the Doppler effect, for a star and an observer endowed with *any inertial motion*, will be

$$D = \frac{\cos^2 \sigma / \gamma}{1 \mp \sqrt{1 - \frac{\cos^2 \sigma}{\gamma^2} \left(1 + \frac{p^2}{R^2 \sin^2 \sigma}\right)}} - 1. \quad (8)$$

For  $p=0$  our previous formula (1), relating to the sub-case of radial motion, reappears. The integration constants  $\gamma$  and  $p$ , whose values may vary from star to star, are originally defined by (6 c). They may be conveniently expressed in terms of the shortest distance  $r_m = R\sigma_m$  and of

$$v_m = \left( R \sin \sigma \frac{d\theta}{dt} \right)_m,$$

the velocity of the star at the perihelion. If  $\beta_m$  is written for  $v_m/c$ , we have

$$p = \frac{R\beta_m \sin \sigma_m}{\sqrt{\cos^2 \sigma_m - \beta_m^2}}, \quad \gamma = \frac{\cos^2 \sigma_m}{\sqrt{\cos^2 \sigma_m - \beta_m^2}}, \quad (9)$$

and, for the semi-amplitude  $\theta_p$  of the orbit,

$$\tan \theta_p = \frac{\beta_m}{\sin \sigma_m}. \quad (9a)$$

The upper and the lower signs in (8) correspond to a motion which, at the moment of observation, is receding or approaching respectively. Introducing  $v_r$ , the radial velocity component at the moment of observation, we may write equivalently, by (6 a),

$$D = \frac{\cos^2 \sigma}{\gamma \left[ 1 \mp \frac{v_r}{c} \sec \sigma \right]} - 1. \quad (8')$$

Finally, notice that at the perihelion, where  $v_r=0$ , the last equation gives, by the second of (9),  $D_m = \sqrt{\cos^2 \sigma_m - \beta_m^2} - 1$ , which is, in both  $\sigma_m$  and  $\beta_m$ , a second-order effect, as might have been expected. That this effect is negative or a blue-shift, need not surprise us. For, the source being at

\* Which "instant" in all actually interesting cases (clusters, etc.) unfortunately extends over a hundred and more hours, this being the most serious difficulty of procuring the requisite data.

its perihelion at the moment of observation, it manifestly was approaching us at the instant of emission.

Thus far the rigorous spectrum-shift formula. Turning to practical applications, we can at any rate confound  $\gamma$ , as external factor in (8) or (8'), with unity. For in all cases of actual interest  $\beta_m^2$  and  $\sigma_m^2$  are negligible in presence of 1. The same remark applies to  $\sigma$  as entering through  $\cos^2 \sigma$  in the numerator and through  $\sec \sigma$  as factor of  $v_r$  in (8'). We are thus left with

$$D = \left(1 \mp \frac{v_r}{c}\right)^{-1} - 1,$$

and since  $v_r^2/c^2$  is again a negligible fraction of unity, our formula ultimately becomes

$$D = \pm \frac{v_r}{c}, \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

which has the appearance of the classical Doppler formula. If we retain this as our working formula, the only innovation consists in  $v_r$  being a function of distance, namely, by (6a), to the required degree of approximation,

$$\left(\frac{v_r}{c}\right)^2 = 1 - \frac{1 - \sigma^2}{\gamma^2} \left(1 + \frac{p^2}{\gamma^2}\right),$$

where, by (9),

$$\frac{1}{\gamma^2} \doteq 1 + \sigma_m^2 - \beta_m^2,$$

and similarly for  $p^2/\gamma^2$ .

Thus, ultimately, our working formula will be

$$D^2 = \left(1 - \frac{r_m^2}{\gamma^2}\right)(\sigma^2 + \beta_m^2), \quad . \quad . \quad . \quad (10)$$

with the previous coordination of the signs, or

$$v_r^2 = \left(1 - \frac{r_m^2}{\gamma^2}\right)(c^2 \gamma^2 + v_m^2).$$

Notice that, to this degree of approximation, the name "radial velocity" given to the measured spectroscopic effect  $cD$  continues to be a perfectly correct one.

For  $r = r_m$  formula (10) gives at once  $D_m = 0$ , the transversal effect as one of the second order being already neglected. Finally, the special case of radial motion follows from (10). In fact, for a star passing through the observer's station we have  $r_m = 0$  and  $v_m = v_0$ , so that

$r^2 D^2 = c^2 \sigma^2 + v_0^2$ , and for one not passing,  $v_m = 0$ ,  $\sigma_m \neq 0$ , and  $D^2 = \sigma^2 - \sigma_m^2$ , as before.

This settles all questions concerning our approximate formula (10), which for the time being differs but imperceptibly from the rigorous equation (8).

Turning now once more to the actual determination of the curvature radius, let us first put together the previous ten pairs of data, noticing, however, that the distance estimate of the Magellanic Clouds has been considerably increased in Shapley's last bulletin\*, and adding three more items concerning globular clusters. The latter were originally discarded as showing the suspiciously small radial velocities, 10, 0, and -10, with a P.E. of 25 to 50 km./sec. Now, however, in view of the possibilities afforded by the amplified formula, there is no reason for excluding them. This makes in all thirteen pairs of data  $r$ ,  $D$ , which, to the best of my knowledge, exhausts all the existing material †. The radial velocities  $cD$  are given in km./sec., and the distances  $r$ , all due to Shapley, in kiloparsecs. The globular clusters are labelled by their N.G.C. numbers (New General Catalogue, *Mem. R.A.S.*, vol. xlix.). The Lesser and the Greater Magellanic Clouds are distinguished by *L.* and *Gr.*

Radial Velocities and Distances of Eleven Clusters and Two Clouds

Object	$cD$	$r$	$r :  D $
6205 .....	-300	11.1	11,000
6341 .....	-160	12.3	23,100
6218 .....	+160	12.4	23,250
*5904 .....	+10	12.5	*
5272 .....	-125	13.9	33,400
7078 .....	-95	14.7	46,400
*7089 .....	-10	15.6	*
*6626 .....	0	18.5	*
5024 .....	-170	18.9	32,200
6333 .....	+225	25.0	33,300
L. Mag. Cl. ....	+150	25.0	50,000
6934 .....	-350	33.3	28,500
Gr. Mag. Cl. ...	+276	35.0	38,000

\* Bulletin 796, Harvard College Observatory.

† The data for a few more clusters may soon be available.



The three clusters showing exceptionally small effects are marked with asterisks. From the nil-effect of the last of these we can conclude only that this cluster is just passing through its perihelion. Similarly, for the remaining two, that they are comparatively near their perihelia, *i.e.* that their  $r/r_m$  differ but little from unity. If so, then the second term in (10) can be neglected and we can write  $D^2 = 2r(r - r_m)/R^2$ . Thus, if the transversal motions of these clusters were observed,  $r_m$  could be estimated and  $R$  could be determined from either cluster. But the proper motions of these distant objects not being accessible to observation, no  $R$ -estimate whatever can be based on these clusters taken by themselves.

With the exception of these three objects the values of the quotients  $r : |D|$ , again in kiloparsecs, are tabulated in the fourth column. If, as in the first paper,  $\beta_m^2$  and  $r_m^2$  were disregarded, these quotients would represent rough approximations to the  $R$ -value, with an arithmetical mean of the ten values  $R = 31,900$  kiloparsecs or

$$R = 6.6 \cdot 10^{12} \text{ astr. units.} \quad (11)$$

But since there are no good reasons for neglecting either  $\beta_m^2$  in presence of  $\sigma^2$ , or of  $r_m$  in presence of  $r$ , any such "mean"  $R$ -value can claim no more than a provisional validity.

A more satisfactory method of estimating the curvature radius, by means of all the data gathered in our table, seems to be the following one.

Since both  $\beta_m$  and  $r_m$ , integration constants, are independent of the actual distance  $r$  of a celestial object, their values and therefore also those of  $r_m/r$  and  $\beta_m^2$  may be reasonably expected to have a random distribution over a group of objects picked out haphazardly, though all equidistant or nearly so. The means  $\beta_m^2$  would then be the same for two such groups, with different values of  $r^2$ , provided each group contains a large number of objects. If so, and if all values of  $r_m/r$  from 0 to 1 are considered equally likely, then formula (10)—applied to the two groups, 1 and 2, say—will give at once

$$D_2^2 - D_1^2 = \frac{2}{3R^2} (r_2^2 - r_1^2), \quad (12)$$

an equation for  $R$  in terms of actual distances and spectroscopic effects alone. Our thirteen objects are certainly too few to form only one such group. With the generous aid of friendly astrophysicists, I hope to gather in the near future

sufficient data for a somewhat reliable application of this statistical method. In the meantime, we cannot do better than split our scanty material into two groups, of *seven* and of *six* celestial objects, as shown by the horizontal line drawn across our table. This gives, in squared km./sec. and squared kiloparsecs,

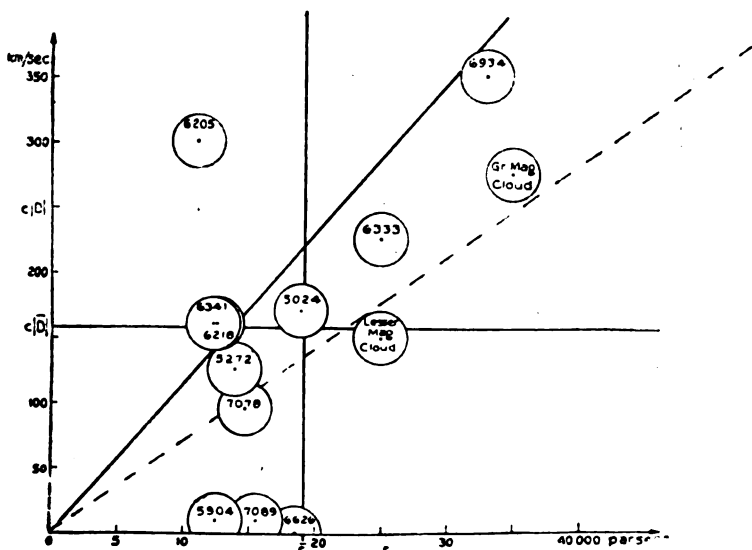
$$\overline{r_1^2} = 176.8, \quad \overline{r_2^2} = 713.9; \quad c^2 D_1^2 = 23,720, \quad c^2 D_2^2 = 50,120,$$

where, of course, no more than two or three figures are at all reliable, and, by (12),  $R = 34,900$  kiloparsecs or

$$R = 7.2 \cdot 10^{12} \text{ astr. units, } \dots \dots (12a)$$

which is somewhat greater than the value (11), but seems at any rate to deserve a higher degree of confidence.

RADIAL VELOCITIES & DISTANCES OF ELEVEN GLOBULAR CLUSTERS & THE MAGELLANIC CLOUDS



In addition to this, a graphical representation of the whole available material has seemed desirable. This is given in the accompanying diagram, in which the thirteen points (centres of labelled circles) have for their coordinates  $r, c | D |$  the pairs of data of the preceding numerical table. The supplementary axes are drawn through the point, near "N.G.C. 5024," whose coordinates are the means of those of the thirteen representative points. That there is at all a correlation of the type: radial velocity increasing on the whole with distance, is shown well enough by the scarcity

or almost complete absence of points in the second and the fourth quadrants, in accordance with a well-known correlation criterion. The dotted line drawn through the origin has the equation  $|D| = r/R$  with  $R = 7.2 \cdot 10^{12}$  astr. units, as in (12a), and this value of the curvature radius is, thus far, supported markedly enough by the tendency of crowding along this line, shown by six or perhaps eight celestial objects. The full line is superfluous in the present connexion.

Rochester, N.Y.

June 1, 1924.

*Note added in proof-reading, August 19.*

Since the above was printed, my attention was drawn to a fairly reliable distance estimate of the spiral nebula Messier 33, of known radial velocity, and Prof. V. M. Slipher was kind enough to give me his unpublished radial velocities of seven more globular clusters, the distances of which were already measured by Shapley. This has enabled me to add to the above correlation table eight more items. The complete table of 21 objects, containing a considerably strengthened evidence for a curvature radius of 7 to  $8 \cdot 10^{12}$  astr. units, was shown in connexion with a paper read at the recent Toronto meeting of the British Association, and will be given, together with a full numerical discussion, in a later issue of this Journal.

LXIII. *A New Variety of Spectra.* By WILLIAM HAMILTON McVICKER, JOSEPH KENNETH MARSH, and ALFRED STEWART\*.

WHEN an induction-coil discharge is passed through the vapours of carbon compounds, decomposition ensues; and the spectra emitted are merely those of carbon or its oxides. By selecting specially stable hydrocarbons and derivatives, Wiedemann and Schmidt† succeeded in obtaining spectra of continuous emission in the case of ten carbon compounds; but as they were unable to extend their work to other organic substances, and as, further, their examination was confined to the visible region, the results

\* Communicated by Professor Stewart.

† Wiedemann & Schmidt, *Ann. d. Physik*, lvi. p. 29 (1895).

obtained by them brought nothing of much importance to light in this branch of spectroscopy.

By employing a large Tesla transformer instead of an induction coil, and by utilizing a quartz spectrograph, we\* have overcome the difficulties encountered by previous workers and have now obtained a series of spectra, each of which is characteristic of the carbon compound by which it is emitted: and thus a new constitutional property has been added to the list which contains refractive index, magnetic rotation, absorption spectra, etc.

In order to illustrate the results which we have obtained, a description of the Tesla-luminescence spectrum of benzene is given below. An examination of this spectrum was originally made with the help of a Hilger quartz spectrograph, size C; but since these initial results were published † we have re-examined the spectrum with an instrument of greater dispersion; and we have also succeeded, by a modification of the experimental conditions, in identifying certain bands in the extreme ultra-violet which were not detectable by the original method. The figures given in the present paper are thus much more complete than those in the earlier communication.

### 1. Apparatus.

The quartz spectrograph employed was the large size constructed by Bellingham and Stanley, which gives a complete spectrum about half a metre long, taken in three sections. Extra rapid plates of various makes have been used. When the spectrum extends into the visible, Panchromatic plates developed with the help of Desensitol have been utilized for this region of the spectrum. The exposure varies very considerably owing to the different intensities of the spectra of various substances. Thus while benzene requires about fifteen minutes' exposure with an extra rapid plate, the spectrum of anthracene can be obtained in twenty seconds with an ordinary plate, and its intensity appears to be almost the same as that of the background of an iron arc under the same conditions.

The cell in which the vapour is photographed is constructed entirely of quartz, with a plane quartz window at the end of a straight tube which is laid in line with the spectrograph axis. This tube contains an internal electrode formed of a

\* Trans. Chem. Soc. cxxiii pp. 642, 817, 2147 (1923).

† *Ibid.*

glass tube filled with mercury ; and the second electrode is a piece of metal foil wrapped round the outside of the quartz tube. A bulb is blown on to the quartz tube near the window ; and an exit for the vapour is provided at the other end of the straight tube, so that the vapour of the substance under examination (which is volatilized in the bulb) can be rapidly passed through the cell in a continuous current. Electrical heating is applied to the straight tube when high-boiling substances are under examination.

The exit-tube of the cell is connected, through a trap, with a mercury vapour-pump, and this in turn is connected with a motor-driven oil-pump.

The current is supplied by a high-frequency apparatus furnished by the Medical Supply Association, Ltd. It is air-insulated, and its secondary and primary are directly coupled together. It contains seventy coils ; and the primary circuit is variable up to twenty-four coils. There are two leyden-jars of about one litre capacity each. The spark-gap has zinc knobs. With this apparatus, driven by means of a 12-inch induction coil, a steady discharge passes, as in an ozonizer, across the vapour contained in the cell.

Variations of pressure and temperature have been found to exert very minor effects in the case of the benzene spectrum. The discharge passes freely and without decomposing the compound to any extent at pressures of 65 mm. and below. At ordinary pressure the discharge is accompanied by sparks and the benzene decomposes, yielding fragments of the carbon spectrum.

## 2. *The Tesla-luminescence Spectrum of Benzene* \*.

The Tesla-luminescence spectrum of benzene consists of over seventy fine bands, which appear to fall into eight groups. The first two of these—termed Group H and Group G in the annexed table—are apparently incomplete ; and it seems probable that the remaining bands of these groups are of feeble intensity, and are thus blotted out by the absorption of ultra-violet light by the benzene vapour itself.

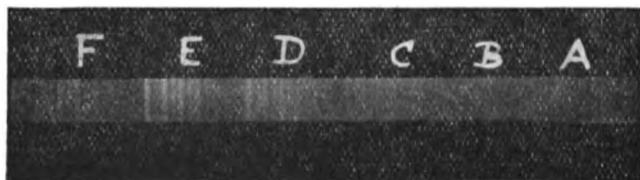
The next group, Group F, contains 12 bands ; then in turn follow Group E—the most complete of all—with 18 bands, Group D with 15 bands, Group C with 12 bands, Group B with 9 bands, and Group A with 5 bands. The brightest series of bands is to be found in Group E ; whi<sup>st</sup>

\* See accompanying figure.

the bands with the lowest wave-numbers in Groups D, C, B, and A become progressively more diffuse and difficult to read. On this account the positions of certain bands in Groups A and B have been read off the plates taken with the Hilger instrument, which shows them most clearly. These figures are given in round brackets in the table.

Some of the bands in Groups G and H were detected in the following manner. Instead of volatilizing pure benzene in the cell, a mixture of benzene and alcohol was placed in the bulb. Alcohol yields no Tesla-luminescence spectrum of its own, but acts in this case merely as a diluent for the benzene vapour. In this way, since the benzene exerts only its partial pressure in the vapour, it was possible to examine its spectrum under higher conditions of rarefaction than could be attained with benzene alone in the cell; and since

Fig. 1.



alcohol vapour is extremely diactinic, we were thus enabled to reduce the degree of light-absorption due to vapour in the cell and so to penetrate further into the ultra-violet region. Figures obtained by this method are shown within square brackets in the table.

In addition to these bands, we have also observed very faint traces of bands in the blue region. These appear to correspond to certain members of a four-group system of twenty-five bands which attain their fullest development in the spectrum of benzaldehyde; but we have not included them in the table since they are so faint that no accurate readings of them are possible. A full list of these bands in the benzaldehyde spectrum has already been given by us in a previous paper\*.

Examination of the table will show that the benzene spectrum exhibits a very apparent regularity. Omitting Groups H and G, which are obviously incomplete, inspection will show that each of the remaining groups contains six

\* Marsh, McVicker, & Stewart, *Trans. Chem. Soc.* cxxiii. p. 2150 (1923).

bright bands (marked with asterisks) ; and it is evident that any one of the strong bands in, say, Group D has a congener in Group C with a wave-number 100 units higher. The same regularity is traceable in the case of the weak bands ; though the completeness of the system is marred by the absence of certain bands from Groups B and C, these bands being possibly too faint to be observed. In Group A the diffuseness of the bands makes it impossible to determine with exactitude whether any faint bands exist or not ; and in this group the readings are at best only approximate ones for the same reason.

*The Wave-numbers of the Bands in the Tesla-luminescence Spectrum of Benzene.*

Group A.	Group B.	Group C.	Group D.	Group E.	Group F.	Group G.	Group H.
					3663*	3765*	[3861*]
—	(3279)*	3372*	3471.5*	3570.5*	—	—	
				3584.5			
(3194)*	(3294)*	3389*	3486.0*	3586.0*	3685.0	—	
—	—	—	3492.0	3588.5	3692.0	—	
				3597.3	3699.0		
—	—	3401.0	3500.0	3599.0	3700.5		
			3503.3				
(3211)*	(3308)*	—	3507.0*	3608.0*	3710.0*	—	
—	3319.0	3419.0	3517.0	3616.0			
(3229)*	3322.5*	3421.0*	3529.0*	3618.5*	3716.0	—	[3914]
—	—	3424.0	3523.5	3624.0	3724.0		
				3625.0			
—	3334.0	3434.0	3534.0	3632.0	3732.0	—	[3931]
(3242)*	3336.5*	3436.0	3536.0*	3635.0*	—		
—	—	3439.5	3539.0	3641.0	3740.0	[3839.0]	
				3643.0		[3843.0]	
—	3351.0	3450.5	3550.0	3649.5	3749.0		
				3651.0		[3852.0]	
(3257)*	3354.0*	3454.0*	3553.0*	3654.0*	3753.0*		
—	—	3456.0	3556.0	—	—		

Figures in square brackets represent bands visible only when benzene vapour is mixed with alcohol vapour. Figures in round brackets were read from plates taken with a Hüller (c) spectrograph ; these bands are very diffuse and hence their position can only be given approximately. The whole spectrum increases in brightness from top to bottom of the table.

The existing data, however, are quite sufficient to suggest that the Tesla-luminescence spectrum of benzene in its main outlines consists of a series of at least eight band-groups, each of which reproduces with great exactitude the same system of bands and differs in position from its neighbours by approximately 100 units in its wave-numbers.

### 3. *The Fraunhofer Effect.*

Hitherto, the Fraunhofer effect has been confined to the cases of the vapours of elements such as sodium; but the discovery of the Tesla-luminescence spectrum of benzene has led us to an extension of this field into the spectra of compounds of complicated structure.

Hartley\* examined the absorption spectrum of benzene vapour at various temperatures and pressures, and embodied his results in a map on which he plotted the positions of the various absorption bands observed by him. It has already been pointed out that owing to the diffuseness of certain bands in the Tesla-luminescence spectrum of benzene, absolute exactitude in measurement cannot be attained; and the same may be said of the determinations of position of absorption bands in benzene vapour. Nevertheless, even when all due allowance is made for this, it must be admitted that the positions of the two sets of bands coincide so closely as to show that each absorption band has a counterpart in one of the emission bands of the Tesla-luminescence spectrum. The following table contains the wave-numbers

Tesla Emission Bands.	Hartley's Absorption Bands.	Tesla Emission Bands.	Hartley's Absorption Bands.	Tesla Emission Bands.	Hartley's Absorption Bands.
3763	3761	3700	3700	3643	****
3753	3754	3699	****	3641	****
3749	3749-52	3692	3691	3635	****
3740	3738	3685	3683	3632	****
3732	3734	3663	****	3625	3621
3724	3722	3654	3656	3618	3617-18
3716	3716	3651	3650	3616	****
3710	3708	3649	****	-	-

of all the emission bands marked by Hartley on his map; and alongside of them we have placed the wave-numbers of all the emission bands observed by us in the same region

\* Hartley, Phil. Trans. ccviii. A. p. 384 (1908).



of the spectrum \*. Inspection will show at once that the figures in the two columns are identical within experimental error in practically every case.

With regard to the missing bands in the absorption spectrum, the positions of which are indicated by the asterisks, it may be pointed out that, although Hartley gives no bands in these positions on his map, an examination of the fuller tables included in his paper shows that he observed regions of absorption even at these points: so that the coincidence between the two sets of figures is even closer than appears from the table above.

The interpretation of these results admits of no doubt. The Tesla-luminescence spectrum of benzene vapour evidently represents a reversal of the absorption spectrum; so that for the first time it has been possible to exhibit the Fraunhofer effect in the case of a complex organic compound of known constitution. In view of the regularity of the benzene Tesla-luminescence spectrum, this seems to mark the opening of a very promising chapter in spectroscopic work; and it suggests that in future a mathematical treatment of absorption spectra may be possible from an entirely fresh point of attack.

#### 4. *Fluorescence and Tesla-luminescence.*

A very complete examination has been made † of the fluorescence spectrum of benzene vapour excited by a mercury vapour-lamp. It was found that there was a very marked resemblance between the fluorescence spectrum and the Tesla-luminescence spectrum. The former is, however, much longer than the latter, as it penetrates further into the ultra-violet; and, further, the development of the so-called "blue bands" in the visible is much greater than in the case of the Tesla-luminescence spectrum, where they are so faint as to be detectable only with difficulty. It was found that some bands were developed in the fluorescence spectrum under a pressure of 60 mm., whereas in the case of the Tesla-luminescence the pressure had to be reduced to less than 2 mm. before the same bands appeared.

\* The absorption spectrum extends into the far ultra-violet, whilst the Tesla-spectrum runs further towards the visible than the absorption spectrum does. Comparison is, of course, possible only in the spectral region in which the two spectra overlap each other.

† McVicker & Marsh, *Trans. Chem. Soc.* cxxiii. p. 820 (1803); Marsh, *ibid.* p. 3318.

### 5. *The Influence of External Conditions.*

Marsh and McVicker\* have investigated the effect of altering the temperature and pressure at which the benzene vapour is examined; but it was found by them that even when these factors were varied over wide ranges the essential characteristics of the benzene spectrum remained unchanged. Alterations in the tuning of the Tesla transformer were also found to have no particular results.

It has already been pointed out above that when benzene is mixed with another substance which yields no Tesla-luminescence spectrum of its own, the benzene spectrum remains unaltered.

McVicker has investigated the effect of a powerful magnetic field upon the Tesla-luminescence spectrum of benzene, but so far the results have been negative, no change having been observed.

### 6. *The Tesla-luminescence Spectra of other Compounds.*

Up to the present we have examined the Tesla-luminescence spectra of over sixty compounds of the most varied character, and it is possible to say that each compound has its own special characteristics, so far as this emission is concerned. We have succeeded in drawing up certain general rules which appear to be valid with regard to the effects produced by changes in the constitution of compounds.

Saturated hydrocarbons, such as cyclohexane, seem incapable of yielding luminescence spectra, and the saturated fatty alcohols appear to show no emission. Aliphatic ketones and aldehydes emit a continuous faint spectrum between the wave-lengths 3500 and 4800, each compound having a spectrum of its own. Substitution in the benzene nucleus may produce either of two effects. If the substituent be a halogen atom or a nitrogroup, the benzene spectrum is completely blotted out and the compound shows no emission whatever; but if the substituent be a hydrocarbon radicle like the methyl group, or an amino-radicle, or an unsaturated group like  $-CHO$ , then the benzene spectrum is subjected to profound modification, whilst at the same time a fresh zone of emission appears in or near the visible. In the case of hydrocarbons containing condensed ring-systems like naphthalene or anthracene, the emission may become very intense and appear quite far up in the visible. Some

\* Marsh & McVicker, *Trans. Chem. Soc.* cxiii. p. 817 (1923).

heterocyclic compounds like pyridine, pyrrol, and thiophen, yield no emission spectra so far as our experience goes; though quinoline, isoquinoline, and tetrahydro-quinoline all yield spectra of varying intensities. It may be pointed out that in each of the last three cases a benzene nucleus is present in the molecule; possibly it forms the luminescent centre.

A large part of the apparatus used in this research was purchased from the Heron Fund of this University, and we wish to express our thanks to Mr. F. A. Heron, D.L. We also desire to acknowledge the assistance received from the Research Committee of the Chemical Society in the form of a grant.

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Northern Ireland.

LXIV. *Application of a Thermionic Valve to the Measurement of the Damping of Vibrations of a Steel Wire.*  
By FLORENCE M. CHAMBERS, M.Sc., Senior Demonstrator  
in Physics, Queen's University, Belfast\*.

*Introduction.*

IN the following will be found the results of some experiments on the damping of forced vibrations of a steel piano-wire, a question about which there seems to be little, if any, quantitative information available.

The idea is to get numerical values for the coefficient of the damping term in the equation of motion, and to examine its variation with pitch and with the method of supporting the wire.

The method employed was to measure the amplitude of forced oscillations under an impressed alternating force furnished by the oscillating current in the circuit of a thermionic valve.

As will be shown, the string was made to vibrate in a simple harmonic manner, and the results obtained apply to the damping of simple harmonic oscillations.

\* Communicated by Professor W. B. Morton.

*Theory of the Method.*

The equation to damped, forced simple harmonic vibrations is

$$\ddot{x} + k\dot{x} + n^2x = C \sin mt$$

assuming friction proportional to velocity, where

$m/2\pi$  = frequency of impressed force,

$n/2\pi$  = natural frequency of the system.

From this equation we find

$$A^2 = C^2 / \{(n^2 - m^2)^2 + k^2 m^2\},$$

where  $A$  is the amplitude of the forced vibration.

$A$  is maximum when  $(n^2 - m^2)^2 + k^2 m^2$  is minimum, i. e. when  $m^2 = n^2 - \frac{1}{2}k^2$ .

Therefore at maximum

$$A^2 = C^2 / \{k^2(n^2 - \frac{1}{4}k^2)\}.$$

The ratio

$$\begin{aligned} A^2 / A_{\max}^2 &= k^2(n^2 - \frac{1}{4}k^2) / \{(n^2 - m^2)^2 + k^2 m^2\} \\ &= a^2, \text{ say;} \end{aligned}$$

$$\therefore a^2 = (1 - \frac{1}{4}k^2/n^2) / \{m^2/n^2 + (1 - m^2/n^2)^2 / (k^2/n^2)\}. \quad (1)$$

As will be seen later,  $k/n$  is of the order from .001 to .0005 for a steel lathe-bed, and from about .003 to .001 for wooden sonometers, so the quantity  $\frac{1}{4}k^2/n^2$  may be neglected compared with 1.

It is then found from above equation that

$$k/n = a(1 + m/n)(1 - m/n) / \sqrt{1 - a^2 \cdot m^2/n^2}.$$

But  $m/n$  is approximately in actual cases equal to 1. (It ranges from .996 to 1.004.)

Therefore  $1 + m/n = 2$  and  $a^2 m^2/n^2 = a^2$ ;

$\therefore k/n$  is very nearly

$$2a(1 - m/n) / \sqrt{1 - a^2}. \quad (2)$$

*Plan.*

Two ways were adopted for finding the  $k/n$  of the string in different circumstances:—

(1) Values of  $a$  were assumed and the corresponding values of  $m/n$  worked out for each of a series of assumed values of  $k/n$ . A set of  $m/n$  and  $a$  curves was plotted from

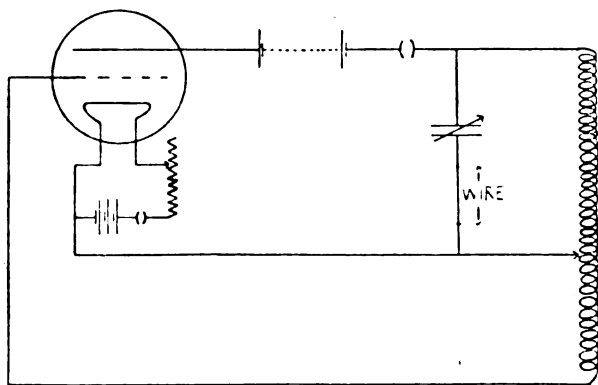
these for the different values of  $k/n$ , and the observed points were plotted on the same paper. Thus it was possible to find approximately the range of  $k/n$  for a given set of results. This method was used in the initial experiments, where, owing to necessary experimental difficulties, great accuracy of observation was not possible.

(2) From the observed corresponding values of  $a$  and  $m/n$ ,  $k/n$  was worked out, using equation (2), and the mean  $k/n$  for each set of observations found. This method was applied to the more accurate observations taken on a steel lathe-bed.

#### *Experimental arrangement.*

The simple harmonic vibrations were maintained by using the oscillatory current in the circuit shown (fig. 1),

Fig. 1.



with the string in series with the condenser, so that the oscillating current passed through the string. The latter was placed between the flat poles of an electromagnet specially made for the purpose and run off the town mains (direct current). The variable coil was also specially made of large self-inductance, with a movable core of iron wires, so that low frequencies could be obtained. The pitch of the oscillating circuit was changed by varying the condenser and varying the number of turns in the secondary and primary coils. Fine adjustments in pitch could be made by moving the iron core.

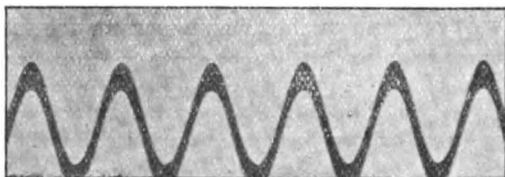
Throughout the experiments on wooden sonometers placed horizontally, there were always variations of amplitude taking place in the course of observations, and these made

accurate readings difficult. The worst variations were abolished by substituting a battery of small accumulators for the unreliable town-mains to supply the anode voltage. The small changes which remained depended on small changes in tension of the wire, due probably partly to friction in the pulley and small yielding of supports, partly to small temperature changes in the wire on account of the current passing through. Once the oscillating circuit has settled down, a galvanometer shows that the current keeps constant throughout an experiment; so the small changes in amplitude are not a result of a varying applied force.

*Test of Simple Harmonic Character of Vibration.*

The vibration form of the string was first investigated by mounting the string in a dark room and photographing on a moving plate the motion of the string's shadow across an illuminated slit, after the manner of Krigar Menzel and Raps. This gives the displacement-time curve of a point on

Fig. 2.



the string. The photograph (fig. 2) is an example of the curves obtained at different points of the string with different positions of the electromagnet. All the photos taken showed curves of the same form.

On measuring up an enlargement of one of these photos, plotting out the numbers obtained, and comparing the resulting curve with a sine-curve of the same size, the two were found to coincide almost exactly.

Several sine-curves were also obtained by plotting the amplitude (measured by the eyepiece-scale of a microscope) against the distance from one end.

The above shows that we are justified in assuming that the vibrations of the string are simple harmonic.

*Method of taking observations.*

As we have now at our disposal a method of forcing the string to vibrate in a simple harmonic manner, and as

the pitch of the oscillations in the circuit is adjustable to any value,  $k/n$  may be found as follows:—

The string and the oscillating circuit are tuned to a pitch about four vibrations per second above or below the pitch of a standard fork. A series of corresponding amplitudes and pitches are found; the amplitude is observed on the eyepiece-scale of a microscope. The pitch is found by observing the number of beats per second between the notes of the string and the fork.  $a$  is obtained by dividing amplitude by maximum amplitude;  $m/n$  by dividing frequency by frequency at maximum amplitude.

$k/n$  is then found as explained from equation (2).

#### *Details of Experiments.*

The first experiments were made on two wooden sonometers, placed horizontally on the bench. The string used was 29 s.w.g. piano-wire, about 60 cm. long. The string vibrated in a vertical plane.

Sonometer A had a screw for adjusting tension of the wire. With Sonometer B the tension was adjusted by weights hung from the string, which passed over a pulley. On both sonometers the string passed over two bridges.

The points of the damping curve for A—about 70 in number, taken on different days—were found to lie between theoretical curves corresponding to  $k/n = .0020$  and  $k/n = .0015$ , but nearer the  $.0020$  curve, at a pitch of about 256 vibrations per second. The accuracy of the observations is not sufficiently great under experimental conditions to make it worth while working out  $k/n$  for each point and taking the mean  $k/n$ .

Sonometer A had a crack in the wood, so we might expect the damping to be greater than in the case of Sonometer B. This was found to be actually the case. The points for B at the same pitch lie close to the curve of  $k/n = .0014$ .

Further observations made on Sonometer B, with more precautions, especially in allowing for the string's thickness, gave the result at pitch 256  $k/n = .0015$ , and at pitch 384  $k/n = .0030$ .

A set of observations on the same sonometer at pitch 320 showed  $k/n$  about equal to  $.002$ . In all cases a large number of observations were taken.

Thus it is found with a wooden sonometer that as the pitch increases the ratio of damping factor to frequency also increases. The damping factor,  $k$ , increases very

rapidly with rising pitch. The amplitude of the vibration falls off rapidly with rising pitch, and a one-inch objective had to be used to observe the amplitude at pitch 384.

In order to obtain more accurate results for  $k/n$  than was possible on account of the small and continual changes in amplitude mentioned above, the sonometer was mounted vertically. The string was fastened as before by a peg, passed over a bridge, and at the lower end was a hook, from which weights were hung.

This was first tried on Sonometer B. It was found now that once the oscillating current had settled down to its steady value, the amplitude of the string would remain steadily at the same value for as long as it was left, the small variations in amplitude having disappeared. This confirms the former conclusion that these variations were due to changes in tension.

It was possible now to make accurate observations, and the value of  $k/n$  was worked out for each reading in turn in every case. Henceforward it is found that the mean deviation of  $k/n$  from the mean value of  $k/n$  obtained for any one set of observations varies from about 1 to 5 per cent.

In order to get as clear a mark as possible on the string for observing the amplitude, a scratch was made on the wire with emery paper or a penknife, and this, illuminated by a lamp, gave a sharp bright line seen through the microscope.

For Sonometer B it was found here that at pitch 256  $k/n = .00103$ —considerably less than the value for the same sonometer mounted horizontally. This is to be expected, as in the present case only one bridge is communicating energy from the string to the sound-box. On another day,  $k/n$  at the same pitch for this sonometer was found to be .000813, showing that when we have a freely-suspended weight other factors come into play besides the pitch in determining the damping. This is referred to later, in connexion with a lathe-bed.

The damping of a string mounted on a massive lathe-bed was next investigated. The lathe-bed was mounted vertically on a stand of concrete, whose foundations were in the ground. This gives a very massive support for the string, and one would expect very small damping, as there can be little motion of the ends.

The damping was actually found to be small, and the note heard was so extremely faint (although the string's amplitude was as great as ever) that often one could only hear it properly by placing the ear against the lathe-bed. Some of



the experiments at the lower pitches had to be carried out in the evenings between 8 and 10 P.M., as there was too much noise during the day to hear the beats at all.

Observations were first of all made on the string at pitch 256. The upper end of the string passed over a blunt steel edge, and was fastened to the back of the bed.

It was found that the readings of each set were consistent among themselves, as before (deviation from mean less than 5 per cent.). The damping factor, however, varied from one set to another at the same pitch. It was thought that this might be due to changing the weights; but with the same weight hung on, so as to give the total suspended mass different shapes, the damping factor varied. The table (Table I.) gives some results at pitch 256.

TABLE I.

$k/n \times 10^3$ .....	1.046	.977	.887	.875	.826	.892
Load, in kg. ....	12.4	12.4	9	15.7	13.2	9

Apparently there is no relation between  $k/n$  and the weight, or if there is such a relation it is masked by the change in end-conditions brought about by altering the configuration of the weights with respect to the string.

An attempt made at this stage to find how the damping depended on the pitch was unsuccessful: there was little change in  $k/n$  with rising pitch; such changes as there were were inconsistent with each other; it was impossible to change the pitch without altering the end-conditions sufficiently to account for any change in damping without considering pitch at all.

Readings were as in Table II.

TABLE II.

Note.....	C	D	E	F	F	F	F
$k/n \times 10^3$ .....	.826	.809	.818	1.045	1.059	1.016	.887

The last value for F was obtained after taking off the weights and putting them on differently.

A further attempt was made to keep end-conditions constant by gripping the string between steel chucks. The old trouble of varying amplitude due to small changes in

tension (probably this time entirely due to temperature-changes in wire) reappeared, so much exaggerated on account of the extremely small damping that it was impossible to take readings.

Finally, the only way of approaching the ideal of a string fixed at both ends seemed to be to hang a very heavy single weight on the end of the string, the weight being arranged each time so that its disposition with respect to the direction of vibration of the string should be the same throughout the experiments. The string (this time a thicker wire, 27 s.w.g.) was gripped at its upper end in two steel jaws—part of a fitting belonging to the lathe-bed. The wire was about 90 cm. long, and from the hook at the lower end hung a weight of 20 kg.

The damping was now smaller than ever (probably nearly all air-damping), and the difficulty of maintaining the maximum amplitude for any length of time very great. One may observe accurately the maximum amplitude, but there is great difficulty in observing accurately the exact *pitch* at maximum amplitude. This was found finally by taking the mean of the two pitches at the same amplitude on either side of the maximum. The average of three such values at different amplitudes (*i.e.* the mean of six readings) gives the mean pitch at maximum amplitude.

Readings of amplitude and pitch were taken as described above—six readings in each set,—and the mean value of  $k/n$  obtained. This was done for frequencies C (253), C (259), D (284), E (316), E (323.5), F (337), G (380), A (423), B (477).

The forks used for pitches other than C were not standard forks, and may not be correct to one vibration. This is not a matter of great importance, as in calculating  $k/n$  the *ratio* only of the frequencies of forced and free vibrations appears.

To get a sustained note from the small forks which were not fitted with resonators, in order to count beats easily, each fork was mounted in turn with its prongs at the mouth of an adjustable pipe closed at one end with water. The pipe, tuned to the fork, acted as a very efficient resonator, and after bowing the fork the note could be heard in the room for over a minute.

The results obtained are shown on the two curves. Fig. 3 shows  $k/n$  plotted against the frequency. It will be seen that  $k/n$  decreases at first rapidly, then more slowly with

increasing frequency. Fig. 4 shows  $k$  and frequency. The damping factor  $k$  increases with rising pitch. Fig. 5 shows a characteristic  $a$  and  $m/n$  curve. It was taken for the lathe-bed, at pitch 256, with a weight of 12.4 kg. hung on the string.

Fig. 3.

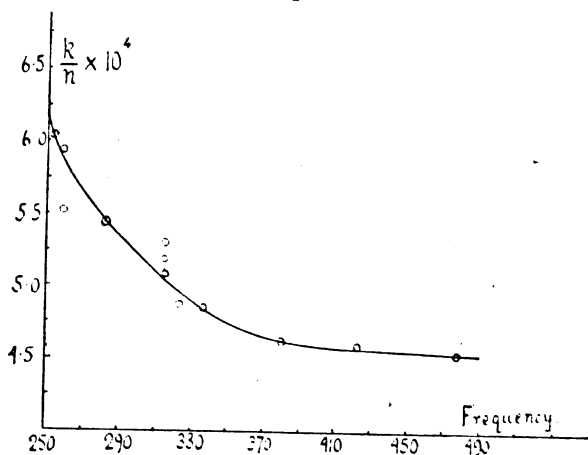
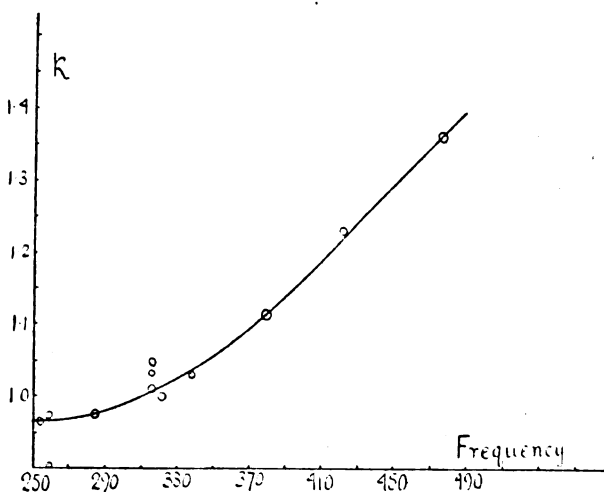


Fig. 4.



#### Summary of Results.

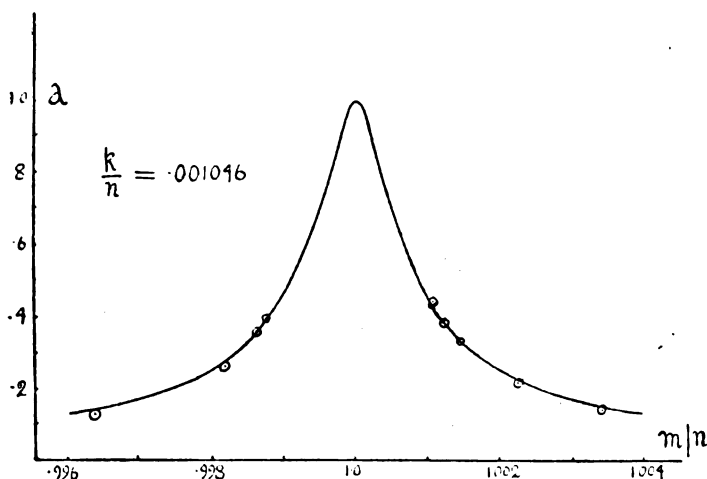
(1) Numerical results have been found for the "damping coefficient" for a steel wire mounted on different supports, and at different pitches.

(2) Damping of a cracked wooden sonometer is greater than for another sonometer without a crack.

(3) For a wooden sonometer, as pitch rises, the factor  $k/n$  increases. There is therefore a very rapid increase of the damping factor  $k$  with rise in pitch.

(4) When the wooden sonometer is mounted vertically, the string passing over one bridge instead of two, the damping is less than with the same sonometer mounted horizontally.

Fig. 5.



(5) For a massive lathe-bed, the string hanging vertically with a weight at lower end, damping of string is very small. Small changes in the configuration of the hanging weights (and so in end-conditions) make considerable differences in results.

(6) Using a very heavy single weight on the string, and keeping its disposition with respect to the string as constant as possible, it was found that  $k/n$  decreased with rising pitch, in contrast to the case of the wooden sonometer.

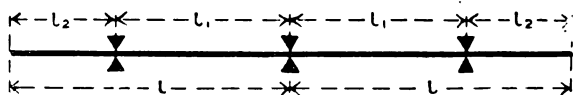
In connexion with the above, I wish to express my grateful thanks to Professor Morton, who suggested the subject of the investigation, and whose help and criticisms have been most valuable throughout; and to Mr. J. Wylie, who designed some special apparatus and whose suggestions on the experimental side have been most helpful.

LXV. *Some Experiments on the Vibration of Bars.* By E. F. RELF, A.R.C.Sc., and W. L. COWLEY, A.R.C.Sc., of the Aerodynamics Department, National Physical Laboratory\*.

THE work described in this paper was undertaken in order to throw light on questions relating to the practical problem of vibration in aeroplane wing spars. Certain spars have been found to give marked vibration troubles through resonance with the engine or with aerodynamic forces over a wide range of frequency. For the sake of simplicity, investigation was confined to the case of a uniform thin beam symmetrically supported at three points. The spars used in aeroplane construction differ from this simple beam in two ways: (a) they are usually tapered, and (b) their depth is so great that the rotatory inertia of the beam elements might have an appreciable effect. These differences do not affect the general arguments of the present paper, but only their direct application to particular cases in practice.

The experiments were conducted upon a brass rod 0.126 in. diameter and 5.09 ft. long; full particulars of the method of experiment are given later in the paper. The frequencies of vibration in the fundamental and in several higher harmonics were calculated theoretically for the general case of a beam supported as in fig. 1, and the results were compared with those of experiment, using the value of  $E/\rho$

Fig. 1.



found by a simpler experiment upon the same rod clamped at one end and free at the other.

It is evident, to begin with, that the frequencies will break up into two systems,—(A) the frequencies of one half of the beam formed by cutting at the centre support and clamping the end so formed, and (B) the frequencies of the same portion but with the clamp replaced by a simple support.

\* Communicated by Mr. R. V. Southwell.

The results are given in figs. 2 and 3 in terms of the quantities  $\phi_1$  and  $\phi_2$ , respectively proportional to  $l_1\sqrt{n}$  and  $l_2\sqrt{n}$ , where  $n$  is the frequency. Fig. 2 shows  $\phi_2$  plotted against  $\phi_1$  for the fundamental and the first four harmonics

Fig. 2.

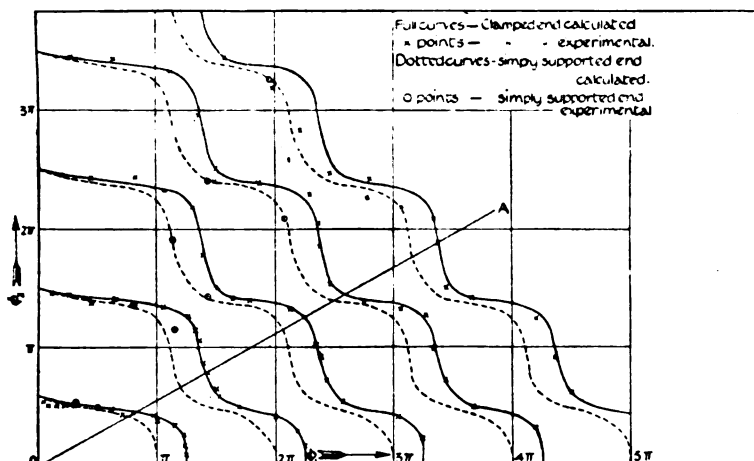
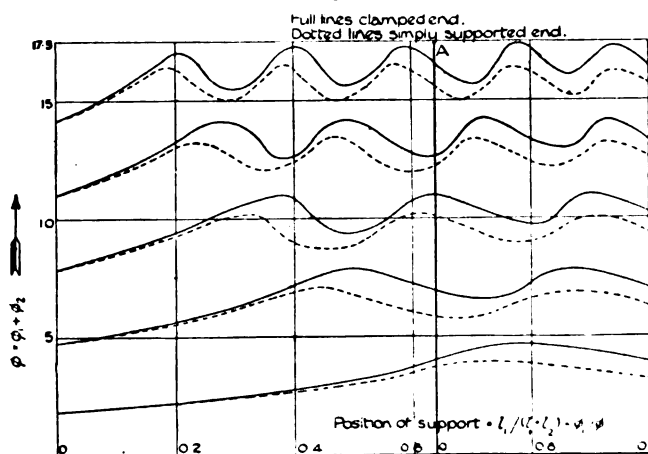


Fig. 3.



as the length ratio  $l_1:l_2$  or  $\phi_1:\phi_2$  is varied, while fig. 3 shows  $\phi = \phi_1 + \phi_2$  plotted against  $l_1/l_1 + l_2$  or  $\phi_1/\phi$  as abscissa.

Thus the square of the ordinate in fig. 3 is proportional to the resonance frequency. In fig. 2 the curves represent calculated values, the experimental results being indicated by crosses and circles, corresponding with full and dotted curves respectively. It will be seen that the agreement is excellent, except as regards the highest harmonic, where the speed of the forcing mechanism used in the experiments was very high, and general vibration impaired the accuracy of measurement. As a further comparison, the positions of the nodes in a particular case were determined and are given against the theoretical values in Table II.

The most interesting feature of the investigation is the tendency, shown in figs. 2 and 3, for the harmonics to group together in certain regions. Thus, a little to the right of the line OA in fig. 3, it will be seen that the first four harmonics occur over a comparatively small range of  $\phi$ , whereas to the left of OA this range is almost doubled. In more complex structures this grouping effect may become even more marked, so that a particular structure may exhibit serious vibration over a considerable range of forcing frequency, whereas a slight modification of design might render it practically free of resonance over the same range.

#### *Theoretical Investigation.*

The case considered has already been described and is illustrated in fig. 1. The results have been expressed in non-dimensional form, so that they may be easily applied to all uniform beams symmetrically supported at three points.

The non-dimensional quantities used are :—

$$\left. \begin{aligned} \phi_1 &= l_1 \sqrt{\left\{ 2\pi n \sqrt{\frac{\rho}{EI}} \right\}} = l_1 \sqrt{\frac{2\pi n}{V_k}}, \\ \phi_2 &= l_2 \sqrt{\left\{ 2\pi n \sqrt{\frac{\rho}{EI}} \right\}} = l_2 \sqrt{\frac{2\pi n}{V_k}}, \\ \text{and } \phi &= (l_1 + l_2) \sqrt{\left\{ 2\pi n \sqrt{\frac{\rho}{EI}} \right\}} = l \sqrt{\frac{2\pi n}{V_k}}, \end{aligned} \right\} \quad (1)$$

where (see fig. 1)

$l_1$  is the distance of an outer support from the centre,

$l_2$  is the length of the overhang,

$l = l_1 + l_2$ , the half length of the beam,

$n$  is the frequency of vibration,

$\rho$  is the mass per unit length,

$E$  is Young's modulus,

$I$  is the moment of inertia of the cross-section about the neutral axis of the section,

$k$  is the corresponding radius of gyration,

$V$  is the velocity of sound along the rod.

The differential equation to be satisfied at every point of the beam (assuming the ordinary beam theory to hold, and neglecting rotatory inertia) is:—

$$\frac{\partial^4 y}{\partial x^4} + \frac{\rho}{EI} \frac{\partial^2 y}{\partial t^2} = 0, \quad \dots \dots (2)$$

which becomes, after writing  $y \sin 2nt$  for  $y$ :—

$$\frac{\partial^4 y}{\partial x^4} - \lambda^4 y = 0, \quad \dots \dots (3)$$

where

$$\lambda^4 = 4\pi^2 n^2 \rho / EI = \phi^4 / l^4. \quad \dots \dots (4)$$

System (A). In this case the condition for resonance can be shown to be:—

$$\begin{aligned} & (1 - \cos \phi_1 \cosh \phi_1)(\sin \phi_2 \cosh \phi_2 - \cos \phi_2 \sinh \phi_2) \\ & = (1 + \cos \phi_2 \cosh \phi_2)(\sin \phi_1 \cosh \phi_1 - \cos \phi_1 \sinh \phi_1). \end{aligned} \quad (5)$$

If  $\phi_1$  and  $\phi_2$  are both large but not equal, a sufficient approximation is given by:—

$$\tan \phi_1 = 2 - \tan \phi_2. \quad \dots \dots (6)$$

The following special cases arise:—

- (1) If  $l_1 = 0$  (beam clamped at one end and free at the other),

$$\begin{aligned} \cos \phi_2 &= -\operatorname{sech} \phi_2, \\ &= 0 \text{ for large values of } \phi_2; \end{aligned} \quad \dots \dots (7)$$

- (2) If  $l_2 = 0$  (beam clamped at one end and simply supported at the other),

$$\begin{aligned} \tan \phi_1 &= \tanh \phi_1, \\ &= 1 \text{ for large values of } \phi_1. \end{aligned} \quad \dots \dots (8)$$



(3) If  $l_1 = l_2$ , and therefore  $\phi_1 = \phi_2 = \phi/2$ ,

$$\cos \phi = 0$$

$$\text{and } \tan \phi/2 = \tanh \phi/2,$$

$$= 1 \text{ for large values of } \phi. \quad \dots (9)$$

System (B). In this case the condition of resonance becomes:—

$$\begin{aligned} & (\sin \phi_1 \cosh \phi_1 - \cos \phi_1 \sinh \phi_1)(\sin \phi_2 \cosh \phi_2 - \cos \phi_2 \sinh \phi_2) \\ & = 2 \sin \phi_1 \sinh \phi_1 (\cos \phi_2 \cosh \phi_2 + 1). \quad \dots (10) \end{aligned}$$

If  $\phi_1$  and  $\phi_2$  are large, we have the approximation:—

$$\tan \phi_1 (\tan \phi_2 - 3) = \tan \phi_2 - 1.$$

The following special cases arise:—

$$(1) \text{ If } \phi_1 = 0, \quad \cos \phi_2 = -\operatorname{sech} \phi_2, \quad \dots (11)$$

this being the same case as (7).

$$(2) \text{ If } \phi_2 = 0 \text{ (beam simply supported at both ends),} \\ \sin \phi_1 = 0 \text{ (excluding } \phi_1 = 0 \text{ as a solution).} \quad \dots (12)$$

The equations (5), (6), (10), and (11) were conveniently solved by taking a series of values for  $\phi_2$  and deducing corresponding values of  $\phi_1$ , the approximate forms (6) and (11) being used when their accuracy was sufficient. The curves of figs. 2 and 3 were then plotted. From either set of curves the resonance frequencies for a given length-ratio  $l_1/l_2$  can be found by drawing a straight line such as OA so that  $\phi_1/\phi_2 = l_1/l_2$ . Using fig. 2, the frequencies are given by

$$n = \frac{\phi_1^2}{l_1^2} \frac{V k}{2\pi} = \frac{\phi_2^2}{l_2^2} \frac{V k}{2\pi}, \quad \dots (13)$$

while in fig. 3 the value of  $\phi$  for abscissa  $l_1/l = \phi_1/\phi$  gives

$$n = \frac{\phi^2}{l^2} \frac{V k}{2\pi} = \left( \frac{\phi_1 + \phi_2}{l_1 + l_2} \right)^2 \frac{V k}{2\pi}. \quad \dots (14)$$

For large values of  $\phi_1$  and  $\phi_2$  the harmonics are separated from their neighbours by intervals of  $\phi_1$  and  $\phi_2 = \pi$  nearly, as can be seen from the approximate forms (6) and (11). Also to a good approximation the separation is  $\phi_1 = \pi$  when  $\phi_1$  is large and  $\phi_2$  small, and  $\phi_2 = \pi$  when  $\phi_2$  is large and  $\phi_1$  small.

The calculated values are given in Table III. for case (A) and in Table IV. for case (B), only the fundamentals and

first harmonics being tabulated. Higher harmonics may be obtained by increasing  $\phi_1$  or  $\phi_2$  by  $\pi$ ,  $2\pi$ ,  $3\pi$ , etc., keeping  $\phi_2$  or  $\phi_1$  respectively constant.

In figs. 2 and 3 the full curves apply to case (A) and the dotted curves to case (B), both systems together giving the solution for the complete beam.

### Experimental Verification.

The brass rod used in the experiments was held in some cases vertically and in others horizontally. At one end the support consisted of an oscillating lever to which the rod was clamped for case (A), and attached by a ball joint for case (B). This lever was connected to an eccentric driven by a small electric motor whose speed could be varied in order to apply forced vibrations of any required frequency to the end of the rod. The movement at the support was of the order of 0.01 inch. The second support for the rod consisted of a slotted steel strip, the slot being bevelled so as not to produce any constraint upon the rod other than that required by a simple support. The position of this support along the rod was varied so as to give a series of values to the length ratio  $l_1/l_2$ .

As the speed of the motor was gradually increased, positions were reached at which marked resonance occurred, the nodes and loops along the rod being clearly seen. These speeds were measured by means of a revolution counter and stop-watch. The fundamental period was too slow for the motor, and was determined by timing the free swings of the rod.

### Comparison between Theory and Experiment.

Before the experimental results can be compared directly with theory the value of  $V$ , the velocity of sound along the rod, must be known. To determine this quantity the movable support was taken away and the rod hung vertically, clamped to the forcing lever. The resonance frequencies were then determined and the corresponding values of  $\phi$  calculated from (7). This led to the results given in Table I.

The ratios  $\phi^2/n$  are constant except at the two lowest frequencies, where the pendulum effect is modifying the results.

TABLE I.

$\phi$ .....	1.87	4.69	7.85	10.99	14.15
$n$ .....	0.808	4.22	11.4	22.1	36.7
$\phi^2/n$ .....	4.33	5.23	5.42	5.46	5.45

Using the highest frequency, we have  $\phi = \lambda l = 14.15$  for  $n = 36.7$ , and inserting the rod dimensions  $l = 5.09$  feet and  $k = 0.0315$  inch, we find that

$$V = \frac{2\pi n}{\lambda^2 k} = 11,370 \text{ ft./sec.}$$

This value was accordingly used in the further experiments to obtain  $\phi$  from  $n$ , the observed frequency.

The positions of the nodes were observed in the simple case of the rod with one end clamped and the other free. They are tabulated below, together with the theoretical values given in Lord Rayleigh's 'Theory of Sound,' and it will be seen that the agreement is excellent.

TABLE II.

Distances of Nodes from Clamped End, expressed as fractions of the length of the rod.

2nd Harmonic	.....	Theory	0.868	0.500	—	—
		Experiment	0.868	0.505	—	—
3rd Harmonic	.....	Theory	0.906	0.644	0.356	—
		Experiment	0.905	0.633	0.354	—
4th Harmonic	.....	Theory	0.927	0.723	0.500	0.278
		Experiment	0.927	0.722	0.508	0.262

TABLE III.

One end clamped and a simple support elsewhere.

(a) Fundamental Curve.

$\phi_1$ .....	3.93	3.93	3.91	3.85	3.70	3.28	2.5	2.22
$\phi_2$ .....	0	0.25	0.5	0.75	1.0	1.25	1.44	1.5
$\phi$ .....	3.93	4.18	4.41	4.60	4.70	4.53	3.94	3.72
$\phi_1$ .....	2.0	1.57	1.5	1.0	0.5	0.25	0	
$\phi_2$ .....	1.51	1.57	1.58	1.67	1.74	1.82	1.84	
$\phi$ .....	3.51	3.14	3.08	2.67	2.24	2.07	1.84	

(b) 1st Harmonic.

$\phi_1$ .....	7.07	7.07	7.06	6.99	6.85	6.48	5.57
$\phi_2$ .....	0	0.25	0.50	0.75	1.00	1.25	1.50
$\phi$ .....	7.07	7.32	7.56	7.74	7.85	7.73	7.07
$\phi_1$ .....	4.89	4.63	4.50	4.42	4.36	4.31	4.25
$\phi_2$ .....	1.75	2.00	2.25	2.50	2.75	3.0	3.25
$\phi$ .....	6.64	6.63	6.75	6.92	7.11	7.31	7.50
$\phi_1$ .....	4.18	4.11	4.00	3.93	3.50	3.83	3.0
$\phi_2$ .....	3.50	3.75	3.86	3.93	4.16	4.00	4.26
$\phi$ .....	7.68	7.86	7.86	7.86	7.66	7.83	7.26
$\phi_1$ .....	2.5	2.0	1.5	1.0	0.5	0.25	0
$\phi_2$ .....	4.33	4.40	4.46	4.53	4.62	4.64	4.71
$\phi$ .....	6.83	6.40	5.96	5.50	5.12	4.89	4.71

TABLE IV.

Simple support at one end and another elsewhere.

(a) Fundamental.

$\phi_1$ .....	3.14	3.13	2.93	2.66	2.02	1.55	1.08	0.76	0.57	0
$\phi_2$ .....	0	0.50	1.0	1.2	1.4	1.5	1.6	1.7	1.8	1.84
$\phi$ .....	3.14	3.63	3.93	3.86	3.42	3.05	2.68	2.46	2.37	1.84

(b) 1st Harmonic.

$\phi_1$ .....	6.28	6.27	5.80	5.19	4.17	3.82	3.62
$\phi_2$ .....	0	0.50	1.0	1.4	1.7	2.0	2.5
$\phi$ .....	6.28	6.77	6.80	6.59	5.87	5.82	6.12
$\phi_1$ .....	3.50	3.38	3.05	2.53	1.32	0.60	0
$\phi_2$ .....	3.0	3.5	4.0	4.2	4.4	4.6	4.71
$\phi$ .....	6.50	6.88	7.05	6.73	5.72	5.20	4.71

TABLE V.—Clamped end.  
Values of  $\phi_1$  (Experimental).

Length ratio $l_1/l_2 = \phi_1/\phi_2$ .	Fundamental.	Harmonics.			
		1st.	2nd.	3rd.	4th.
0.085	0.143	0.384	0.66	0.93	1.18
0.180	0.289	0.810	1.37	1.94	2.49
0.334	0.537	1.44	2.56	3.50	4.16
0.456	0.756	2.02	3.34	4.25	4.44
0.593	0.96	2.56	4.05	4.67	—
0.617	—	—	—	4.74	6.20
0.774	1.232	2.27	4.33	5.80	6.90
1.0	1.58	3.97	4.70	7.18	7.74
1.152	—	4.18	5.16	7.40	8.80
1.224	—	—	—	—	8.74
1.280	1.95	4.26	5.60	7.43	—
1.402	—	—	—	—	9.64
1.600	2.21	4.37	6.66	7.71	10.5
1.788	2.52	4.47	7.09	8.18	10.6
2.28	3.06	4.74	7.36	9.60	10.8
2.58	3.18	4.80	7.50	10.28	11.5
3.36	3.60	5.33	7.63	10.5	13.2
4.72	3.83	6.28	8.06	10.8	13.7
7.28	3.81	6.84	9.55	11.5	14.1
13.13	3.90	7.09	10.22	13.2	16.1
23.6	—	—	—	13.4	16.5

TABLE VI.—Simply supported end.  
Values of  $\phi_1$  (Experimental).

Length ratio $l_1/l_2 = \phi_1/\phi_2$ .	Fundamental.	Harmonics.			
		1st.	2nd.	3rd.	4th.
0.6	1.05	2.56	3.60	4.53	6.17
1.0	1.62	3.60	4.50	6.54	—

LXVI. *The Crystal Structure of Cuprite and Rutile.* By  
GILBERT GREENWOOD, M.Sc., *John Harling Fellow in the  
University of Manchester* \*.

PREVIOUS investigations of both these minerals have been carried out by means of X-rays, and the published accounts would suggest that they are worthy of further investigation. Cuprite is an example of those interesting cases where the symmetry as deduced crystallographically from geometrical considerations is at variance with that assigned to the crystal from an investigation of its structure. The structure described by W. H. and W. L. Bragg ('X-rays and Crystal Structure,' 1924, p. 147) is cubic holohedral, whilst the undoubted holoaxial character of certain crystals is shown by the {986} face, found by H. A. Miers (Phil. Mag. xviii. p. 127, 1884). The position with regard to rutile, which crystallizes in the tetragonal system, is slightly different: the divergence of opinion in this case is as to the correctness of two different proposed structures. Rutile has been investigated by Vegard (Phil. Mag. xxxii. p. 65, 1916) and also by Williams (Proc. Roy. Soc. xciii. A, p. 418, 1917). They both obtained somewhat similar spacings, but Williams found, in addition, two new reflexions occurring at half the first order glancing angles determined by Vegard for the (100) and (111) planes: he also obtained different values for the intensities of the spectra.

The investigation of these minerals now to be described was carried out by the X-ray spectrometric method, the radiation used being the  $K\alpha$  rhodium rays of wave-length 0.615 Å. Attention was particularly concentrated on the measurement of intensities rather than on the accurate determination of glancing angles. The measurement was made in the following manner. A comparatively wide chamber slit was used and a series of readings were made over a range which includes the peak. To make a reading the crystal was swept with a uniform angular velocity through the reflecting angle corresponding to the chamber setting. The total ionization produced in the chamber was measured by adjusting the potential so that the electrometer string returned to zero. This applied potential is then a measure of the quantity of X-rays received in the chamber. On plotting the intensity values thus obtained against the chamber angles a flat-topped peak of the type depicted by

\* Communicated by Professor W. L. Bragg, F.R.S.

Bragg, James, and Bosanquet (*Phil. Mag.* xli. p. 309, 1921) is obtained. From a graph of this type it is very easy to obtain a true measurement of the reflexion alone as distinct from the general radiation. In order to express each reflexion on a common scale, so that they would all be strictly comparable, they were compared directly with the second order reflexion from the (100) planes of rocksalt, measured at once, under the same conditions, and in the same manner. The faces of both the minerals and the rock-salt were large enough to intercept the whole of the incident beam. The error introduced by unequal absorption, due to incorrectly ground faces, was eliminated by making one reading with the crystal reflecting to the right-hand side, and then turning it round so as to reflect to the left-hand side and making a second reading. The mean of these two has been shown by W. H. Bragg (*Phil. Mag.* xxvii. p. 888, 1914) to be the real intensity of the reflected beam. All the intensities are expressed as percentages of the 200 reflexion from rocksalt. Owing to the "extinction factor" effect in measuring particular intensities, the doubt as to the relative scattering powers of the atoms etc., it will be better to seek for an atomic arrangement which gives the best general agreement rather than to try to find an arrangement which gives quantitative agreement for one or two orders. See W. L. Bragg (*Proc. Roy. Soc. A*, p. 34, 1924).

#### CUPRITE.

The results of the measurements made as described above are set out in the following table. The glancing angle for the first order for each face is a mean value obtained from the crystal and chamber settings for all the orders measured on both the right- and left-hand sides. The other values which are given in the first column, and refer to orders higher than the first, have been calculated from the glancing angle.

TABLE I.

Angle.	Sin.	<i>hkl</i> .	I.	log I.	A.	$\frac{I}{A^2}$ .	$\frac{I}{A^3}$ .
5° 49'	0.1014	110	7.2	0.8573	8	0.9	0.0112
7° 8'	0.1242	111	185.5	2.2684	58	3.2	0.055
8° 15'	0.1435	100	110.0	2.0414	50	2.2	0.033
11° 42'	0.2028	220	61.9	1.7914	66	0.94	0.014
14° 23'	0.2484	222	26.0	1.4150	50	0.52	0.010
16° 41'	0.2870	200	18.5	1.2672	66	0.28	0.0043
17° 43'	0.3042	330	—	—	8	—	—
21° 52'	0.3726	333	8.5	0.9294	58	0.147	0.0025
23° 56'	0.4056	440	7.0	0.8451	66	0.106	0.0016
25° 30'	0.4305	300	3.7	0.5682	50	0.074	0.0015

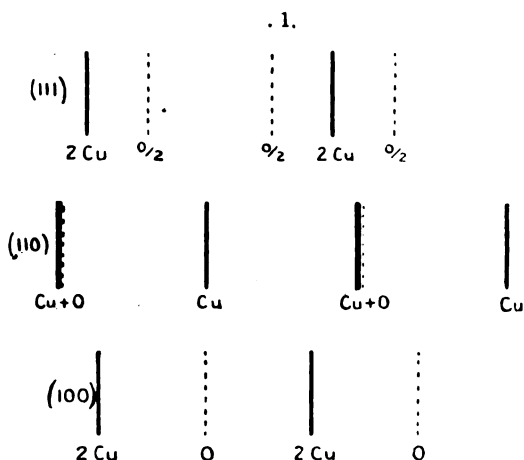
Calculation shows that  $d_{100} = 2.142 \text{ \AA}$ , and that the volume  $d_{100}^3$  contains one quarter of a molecule, *i.e.* two molecules in the larger cube of edge  $2d_{100}$ . This is in agreement with the structure previously found. In this structure the copper atoms lie on a face-centred cubic lattice and the oxygen atoms on a centred cubic lattice of the same dimensions. The oxygen lattice is displaced with respect to the copper lattice in the direction of one of its diagonals for a distance equal to one quarter of the diagonal length. In addition, the small first order reflexion from the (110) planes which had been overlooked in the earlier investigation (see 'X-rays and Crystal Structure,' 1924, p. 145, fig. 53) has now been found. The spacings of the planes are given in fig. 1 and the structure factors by the equation :

$$A_{100} = 58 + 8 \cos n \pi,$$

$$A_{111} = 58 + 8 \cos n \frac{\pi}{2},$$

$$A_{110} = 37 + 29 \cos n \pi,$$

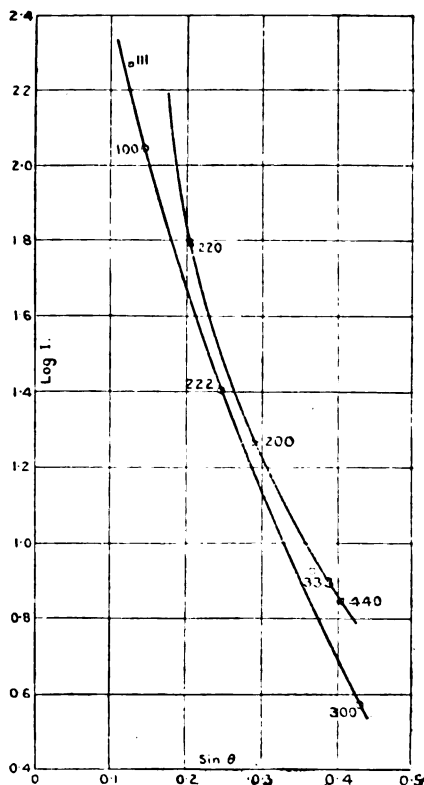
where  $n$  is the order of the spectrum.



The "weight" of a diffracting centre was taken as proportional to its atomic number—29 for Cu and 8 for O. From a consideration of these structure-factors we find that the reflexions can be divided into four groups:—200, 220, and 440, with a factor of 66; 111 and 333, with a factor of 58; 100, 300, and 222, with a factor of 50; and finally 110 and 330, with factors of 8.

It is easy to see that the 110 and 330 reflexions are in agreement with the above: 110 was quite small, and 330 was too small to observe even though 440 was fairly big. It is, however, much more difficult to find even a general agreement among the other spectra, since the factors are all so nearly equal. Fig. 2, in which the logarithm of the intensity is

Fig. 2.



plotted against the sine of the angle of reflexion, shows that this agreement does undoubtedly exist. Reflexions 100, 300, and 222 fall on the lower curve and reflexions 200, 220, and 440 on the upper curve, whilst 111 and 333 lie in between these two curves. It is always of interest to see whether the measured intensities appear to vary as the structure-factor or as its square. Theoretically they might be expected to vary as the square, and this has been found to be the case with some simple structures such as rocksalt. On the other hand, in more complicated structures such as



calcite and aragonite the intensities have been found to vary more nearly as the first power of the factor. In the last two columns of Table I. are given the values of  $\frac{I}{A}$  and  $\frac{I}{A^2}$ .

On plotting these values against the corresponding angle, either set of points fits about equally well on a smooth curve. A reason for this indifference of choice between the structure-factor or its square may possibly be found in the fact that all the factors concerned have very nearly their maximum value.

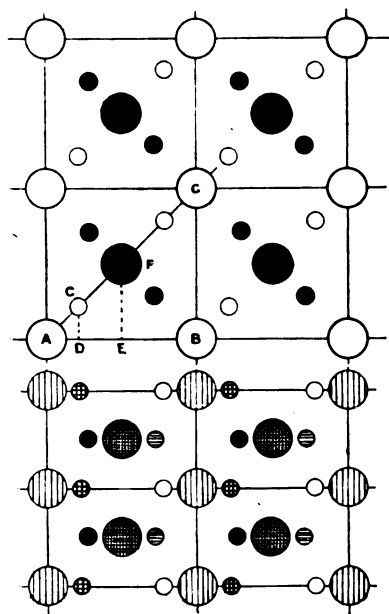
#### RUTILE.

The results obtained in this investigation leave no doubt as to the correctness of Vegard's earlier work. A careful search for the two reflexions described by Williams entirely failed to reveal any trace of them. The result of the intensity measurements was a slight alteration of the one parameter involved in the structure proposed by Vegard. The measurement of the spacing of the (100) planes gave  $d_{100} = 2.29 \text{ \AA}$ , which is in satisfactory agreement with Vegard's value of  $2.26 \text{ \AA}$ . Further determinations of glancing angles were not made, the angles found by Vegard being used throughout the work. Calculation shows that a quarter of a molecule is contained in the cell  $d_{100}^2 \times d_{001}$ , and this suggested that the type of structure was that of a centred prism. This is in agreement with the type of structure deduced by Vegard, which is illustrated in fig. 3. The upper part of the figure is a projection on the plane (001), whilst the lower portion of the figure shows a projection on the plane (100). The large circles represent titanium atoms and the small ones oxygen; circles differently shaded lie in different planes.

The titanium atoms lie on a centred tetragonal lattice, whilst the oxygen atoms are on four simple tetragonal lattices, interpenetrating the titanium lattice in the manner shown in the drawing. The (001) planes contain both oxygens and titaniums, each plane of this series is a repetition of any other one.

If we consider the titanium atoms on a centred tetragonal prism of edges  $2d_{100}$ ,  $2d_{100}$ , and  $2d_{001}$ , we find that it will give spacings for the (100), (110), (101), and (001) planes, which agree with those experimentally found. The spacing for (111) was found to be twice as great as would have been expected. As will be seen later, this is due to the oxygen atoms: the titanium planes parallel to (111) alternately do and do not contain oxygen atoms in addition to the titanium. Hence the spacing is twice the distance between adjacent (111) planes of a centred tetragonal lattice of titanium atoms.

Fig. 3.



The following Table shows the experimental results :—

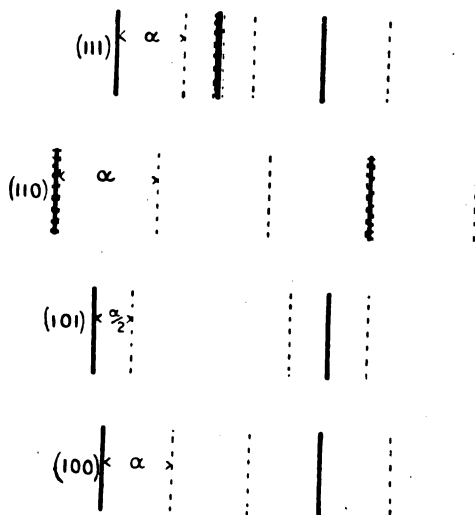
TABLE II.

Angle.	Sm.	$hkl$ .	L.	A.	$A^2$ .	$\frac{I}{A}$ .	$\frac{I}{A^2}$ .
$5^\circ 26'$	0.0947	110	278	24.4	586	11.48	0.474
$7^\circ 4'$	0.1231	101	95.2	16.1	259	5.92	0.404
$7^\circ 41'$	0.1337	100	41.1	10.4	108	3.99	0.380
$8^\circ 5'$	0.1406	111	59.6	13.8	191	4.32	0.312
$10^\circ 55'$	0.1894	220	105	35.6	1268	2.95	0.083
$11^\circ 57'$	0.2071	001	104	38	1442	2.74	0.072
$14^\circ 14'$	0.2459	202	10	10.3	103	0.98	0.098
$15^\circ 31'$	0.2675	200	27	23.1	533	1.17	0.051
$16^\circ 20'$	0.2813	330	40	30.5	935	1.32	0.043
$16^\circ 30'$	0.2840	222	38	35	1228	1.09	0.031
$21^\circ 40'$	0.3692	303	19.6	36.4	1324	0.54	0.015
$22^\circ 18'$	0.3795	440	6.7	22.1	489	0.303	0.0188
$23^\circ 29'$	0.3985	300	10	32.5	1030	0.307	0.0097
$24^\circ 28'$	0.4142	002	18	38	1442	0.473	0.0125
$25^\circ 0'$	0.4226	333	—	2.7	7.6	—	—
$28^\circ 15'$	0.4734	550	7	36.6	1340	0.193	0.0052
$29^\circ 22'$	0.4904	404	3.7	23.1	533	0.160	0.0069
$32^\circ 20'$	0.5349	400	1.8	6.1	38.2	0.295	0.0472
$34^\circ 15'$	0.5628	444	2	22.1	489	0.090	0.004
$38^\circ 25'$	0.6213	003	3.6	38	1442	0.095	0.0025

2 Y 2

The results are of a similar order to those of Vegard, but though the actual values are somewhat different the arguments in favour of a structure on pp. 77-81 of his paper (*loc. cit.*) are still quite valid. The side of the unit cell is  $AB=a=2d_{100}$ . The position of the oxygen atoms—say C—

Fig. 4.



is fixed by a parameter  $\epsilon$  (a fraction of  $a$ ), the length AD being  $\epsilon a$ . The spacings for the various planes are shown in fig. 4, and the corresponding structure-factors are given by

$$\left. \begin{aligned} A_{100} &= 22 + 16 \cos n\alpha, \\ A_{110} &= 30 + 8 \cos n\alpha, \\ A_{101} &= 22 + 16 \cos n\frac{\alpha}{2}, \\ A_{111} &= \frac{1}{2} [22 + 16 \cos n\alpha + 38 \cos n\pi]. \end{aligned} \right\} \quad \dots (1)$$

The connexion between  $\epsilon$  and  $\alpha$  is  $\epsilon = \frac{AD}{AB} = \frac{AD}{2AE} = \frac{\alpha}{4\pi}$ .

The "weight" given to the titanium atoms was 22.

The value of  $\epsilon$  was determined thus:—From the proposed structure it will be seen that the (001) planes would give a normal sequence of spectra. This is borne out by the measured intensities of the first three orders, which are very

similar to those from (100) of rock-salt—a well-known normal sequence. The intensities of all the orders were now plotted against their corresponding angle and a curve drawn through (001), (002), and (003): this gives the normal decrease of intensity with angle. All the other intensities which lie on the graph below this normal curve were expressed as a fraction of the corresponding normal value for that angle. The reflexions were then arranged in a descending series of their fractional sizes. When the true value of  $\epsilon$  has been chosen, the calculated structure-factors should also be in this same order. As previously stated, our object was to choose a value for  $\epsilon$  which gives the best general agreement: the method adopted was very similar to that of A. J. Bradley (Phil. Mag. xlvii. p. 657, 1924). It is very easy by the construction of a few graphs to solve the equations (1) for any value of  $\frac{\alpha}{2}$ . Solutions were obtained for various angles,

and the resulting structure-factors arranged in descending order and compared with the experimentally determined descending series of intensities. The mean error in each case was determined. It showed a well-marked minimum for a certain angle. The results obtained are given in the table.

TABLE III.

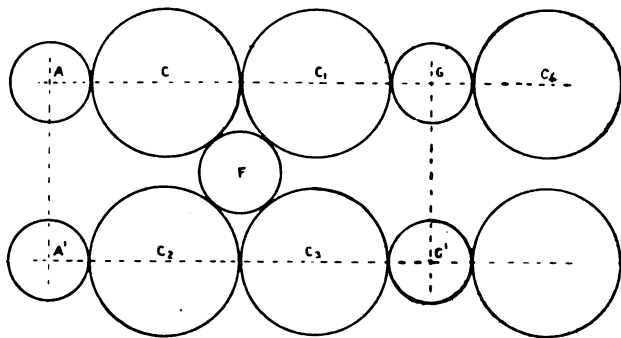
$\frac{\alpha}{2}$	Error.	$\frac{\alpha}{2}$	Error.
100°	3.41	110°	1.65
104°	2.12	112°	1.83
106°	2.0	120°	2.59
108°	1.47		

The value of  $\alpha$  is therefore 216°, and this makes  $\epsilon = 0.300$ . If, now,  $l$  is the length AC of fig. 3, *i. e.* the distance between oxygen and titanium centres, the value of  $l$  works out to be 1.948 Å.

The packing together of the atoms in space must now be considered. In consultation with Professor W. L. Bragg it was decided to attempt to make the spheres, of which structural models are usually built up, of such a size as to represent, more or less, the diameter of electronic orbits of the atoms concerned. From this point of view the metallic element atoms would be smaller than those of the non-metals, not *vice versa* as has been often used in the construction of such models. In the case of rutile the most important

plane is (110), or the line ACFG of fig. 3. The points A, A', G, G', C, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and F of fig. 5 are already fixed as the centres of atoms. As was pointed out by Niggli (*Zeit. für Krist.* lvi. p. 119, 1921) and Jertsch (*Zeit. für Krist.* lviii. p. 293, 1923) in Vegard's original structure, the distances from the oxygen atom C to the two titanium atoms A and F were different, even though the atoms must touch along these two directions, in order to hold the structure together. Owing to the change in the parameter  $\epsilon$  this peculiarity has now disappeared. Calculation shows that  $AC = 1.95 \text{ \AA}$  and  $CF = 1.96 \text{ \AA}$ —a difference of  $0.01 \text{ \AA}$  instead of, as originally,  $0.1 \text{ \AA}$ . Thus, giving the oxygens their largest size, we obtain the length  $CC = 2.58 \text{ \AA}$  as the diameter. The titanium

Fig. 5.

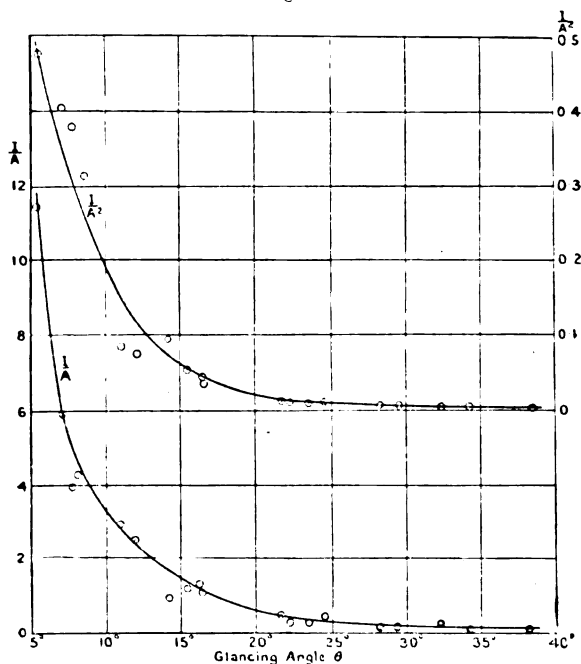


atoms which fit in between the four oxygens  $CC_1C_2C_3$  and in between the two oxygens  $C_1$  and  $C_4$ , then possess a diameter of  $1.32 \text{ \AA}$ . The value  $2.58 \text{ \AA}$  for oxygen is a maximum: it would still be possible to fit the structure together using smaller oxygens and correspondingly larger titaniums. It is again of interest to see whether the measured intensities vary as the square of the amplitude-factor or as the amplitude-factor itself.

In columns 7 and 8 of Table II. are recorded the values of  $\frac{I}{A}$  and  $\frac{I}{A^2}$ . Fig. 6 shows these values plotted against the corresponding angles. An inspection of the curves shows that in the case of smaller angles the  $\frac{I}{A}$  graph is more satisfactory, whilst for larger angles the reverse is true. It

has been found before (see W. H. Bragg, Proc. Phys. Soc. Lond. xxxii. pt. 5, Aug. 1921) that for the larger reflexions the "extinction" factor has a greater influence, decreasing them more than it does the smaller spectra. When this occurs the intensities become more proportional to the structure-factor itself than to its square. Since the greater reflexions occur at the smaller glancing angles, one would expect to find the spectra at these smaller angles varying more as the factor itself. This is what occurs with rutile.

Fig. 6.



Finally I wish to express my indebtedness to Professor W. L. Bragg and Mr. R. W. James for their helpful advice during the course of the work, and also to Miss Lucy Wilson, of Wellesley College, for assistance in the calculations of structure-factors and intensities.

LXVII. *A New Determination of the Constant N of Avogadro, based on its Definition.* By PIERRE LECOMTE DU NOÛY, D.Sc.\*

[From the Laboratories of the Rockefeller Institute for Medical Research, New York.]

[Plate XIII.]

IT has been shown in a previous paper† that it was possible to obtain monomolecular layers of certain colloidal substances, such as sodium oleate, and the technique and instrument used to establish the criterion of the existence of such a layer have been described. It is therefore unnecessary to repeat a description of the experimental work, which has also been dealt with in great detail in the 'Journal of General Physiology'‡ and 'Journal of Experimental Medicine'§.

Subsequent to the writing of the last paper, further experiments were made with pure sodium oleate, especially prepared in this laboratory by Dr. L. Baker; investigations with higher dilutions revealed two other minima of the surface tension at  $1/1,390,000$  and at  $1/1,220,000$ . The purpose of this paper is to explain these new minima, and to apply the data yielded to a determination of the fundamental constant N.

### I.

The apparatus used is shown in Pl. XIII. Series of 24 different dilutions at a time were placed in the standard watch-glasses, in which the total surface of adsorption was 26.4 sq. cm. (diameter of the free surface of the liquid = 4.08 cm., area = 13.08 sq. cm.; maximum depth at the centre = 0.3 cm.; surface of the glass, segment of sphere, 13.33 sq. cm.). Each watch-glass was placed on a bronze ring, levelled by means of three levelling-screws, which could therefore be raised parallel to itself, without jarring, in order to bring the surface of the solution in contact with the ring of the tensiometer. The results of ten series of measurements are given in Table I. Some of the experiments are plotted in Charts I., II., and III.

\* Communicated by the Author.

† du Noüy, P. L., Phil. Mag. xlviii. p. 264 (1924).

‡ du Noüy, P. L., Journ. Gen. Phys. i. no. 5, p. 521 (1919), and July 1924 (vol. vi. p. 625).

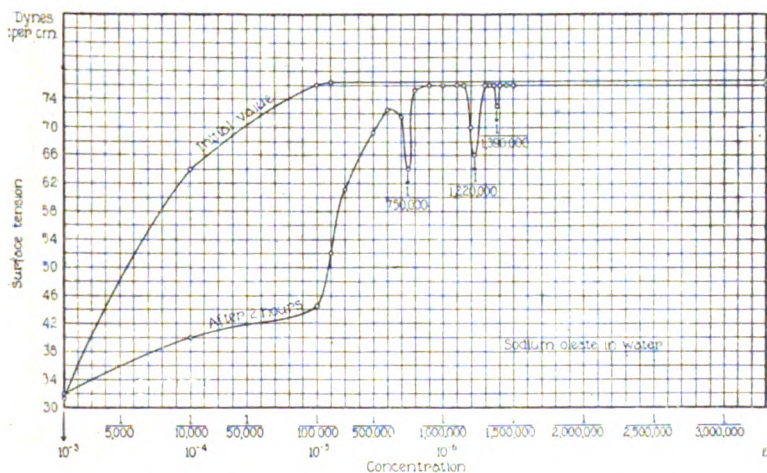
§ du Noüy, P. L., Journ. Exp. Med. xxxv. pp. 575-707 (1922), xxxviii. p. 87 (1923).

TABLE I.

Concentrations at which the 3 minima occurred in 10 series of experiments, in the value of the surface tension of sodium oleate solutions, after 2 hours' standing.

No. of experiment.	First minimum. C <sub>1</sub> .	Second minimum. C <sub>2</sub> .	Third minimum. C <sub>3</sub> .
1 .....	1/750,000	1/1,220,000	1/1,390,000
2 .....	1/750,000	1/1,220,000	1/1,390,000
3 .....	1/749,000	1/1,220,000	1/1,380,000 (?)
4 .....	1/750,000	1/1,222,000	1/1,391,000
5 .....	1/749,000	1/1,220,000	1/1,390,000
6 .....	1/751,000	1/1,222,000	1/1,390,000
7 .....	1/751,000	1/1,222,000	1/1,395,000
8 .....	1/750,000	1/1,220,000	1/1,386,000
9 .....	1/750,000	1/1,218,000	1/1,390,000
10 .....	1/750,000	1/1,221,000	1/1,390,000

Fig. 1.



Surface tension of sodium oleate in water, after two hours, in function of the concentration.

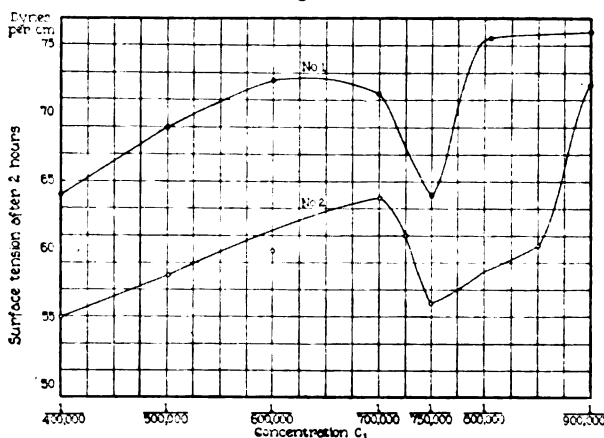
Three decided minima, always occurring at the same concentrations, are observed: one at 1/750,000, the second at 1/1,220,000, and the third at 1/1,390,000.

As a rule, all minima in good experiments occurring exactly at the concentrations 1/750,000, 1/1,220,000, and



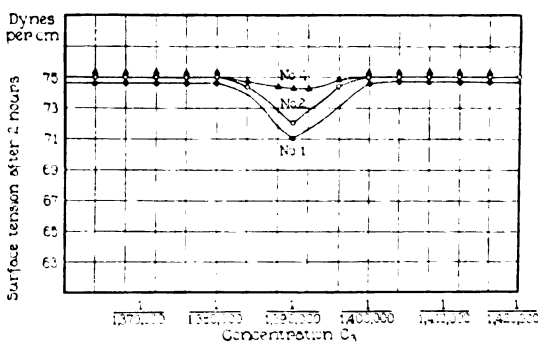
1/1,390,000 are always more marked and larger in absolute value than those occurring at other concentrations near by. No important and well-defined minimum was ever observed, except at these concentrations. It seems that when a displacement occurs it is due either to an experimental

Fig. 2.



Surface tension of sodium oleate in water, after two hours, in function of the concentration.

Fig. 3.



Surface tension of sodium oleate in water, after two hours, in function of the concentration.

accident, or to the impossibility of the molecules to organize themselves so as to produce the minimum field of forces. In such a case the place of the minimum does not mean anything. For this reason, the writer does not believe that a mean value would express the truth more accurately

than can be done by choosing as critical concentrations those at which the minima are more sharply defined and more important in absolute value.

I have pointed out in my previous paper that the minimum at 1/750,000 corresponds probably to the existence of a monolayer of vertically organized molecules. The calculation yielded a figure close enough to the length assumed by Langmuir for the molecule of oleic acid \* to support this view. In the present set of experiments, greater care was taken with the measurement of the total area of the liquid in the watch-glasses, and it was found that the total surface was 26.41 sq. cm. instead of 25.6, as introduced in our first calculations. This error being corrected, the length of the molecule of sodium oleate is now  $12.30 \times 10^{-8}$  cm., assuming that all the molecules are adsorbed. This assumption is a natural and logical consequence of the fact that the length of the molecule of oleic acid is  $11.2 \times 10^{-8}$  cm.; as the Na atom replaces one H atom at the end of the molecule, it is very probable that the length is increased slightly. Should only 10 per cent. of the molecules be free in the solution, then the quantity of substance adsorbed would be smaller, and the length of the molecule would be  $11.2 \times 10^{-8}$  cm. In other words, there would be no change in the length of the molecule of oleic acid after substitution of H by Na. This does not agree with the actual chemical conception of this molecule. Therefore we shall provisionally admit that the molecules are all adsorbed, and that  $12.30 \times 10^{-8}$  cm. corresponds to the length of the molecule of sodium oleate. The increase of length due to the Na atom is then  $1.1 \times 10^{-8}$  cm. (Of course, this represents the projection on the longitudinal axis of the molecule, and not the real distance from the Na atom to the O atom, to which it is linked.)

Let us now consider the second minimum. The same calculation ( $1/1,220,000 \times 2 =$  amount of substance in the watch-glass, divided by the area 26.4, gives the amount per sq. cm. This figure is in turn divided by the specific gravity) yields the thickness of the layer. It is  $7.56 \times 10^{-8}$  cm. This minimum can only occur if a critical organization of molecules takes place. Consequently, in this case, we have another monolayer, but the molecules are horizontally arranged, and  $7.56 \times 10^{-8}$  cm. is one of the dimensions of the base of the molecule.

The third minimum, at 1/1,390,000, corresponds to a third monolayer, the thickness of which is  $6.64 \times 10^{-8}$  cm.

\* R. A. Millikan, J. Am. Chem. Soc. xxxix. (1917).

This is the third dimension of the molecule, which, at this dilution, lies flat on the surface, occupying a rectangular area  $7.56 \times 12.30$  sq. cm.  $\times 10^{-16}$ . [In the second position (at a dilution of  $1/1,220,000$ ) it occupies, in the horizontal plane, an area equal to  $6.64 \times 12.30$  sq. cm.  $\times 10^{-16}$ , and in the first position (vertical molecules, at a dilution of  $1/750,000$ ) it occupies in the horizontal plane an area equal to  $7.56 \times 6.64$  sq. cm.  $\times 10^{-16}$ .] This may be true, regardless of the real shape of the molecule, since we are only concerned with the space occupied by one molecule when symmetrically packed with others.

These three dimensions make it possible now to compute the volume of the molecule, and, knowing the specific weight of the substance (0.821), its mass in grams is found to be  $507 \times 10^{-24}$  gram. By dividing the molecular weight of sodium oleate (304.35) by the mass of one molecule, according to the very definition, we obtain the constant N:

$$N = 6.003 \times 10^{23}.$$

This value agrees within 0.1 per cent. with the value found by Millikan ( $6.062 \times 10^{23}$ ), which he considers as correct within  $\pm 0.006$  †.

From this value of N, one obtains readily the value of the electron ( $4.82 \times 10^{-10}$  U.E.S.) and that of the mass of the hydrogen atom ( $1.677 \times 10^{-24}$  gram). (Instead of  $4.77 \times 10^{-10}$  and  $1.662 \times 10^{-24}$  by Millikan.)

This accord is quite remarkable, considering the extreme simplicity and directness of the method and of the calculation based only on the definition of Avogadro. However, an objection may be raised as to the number of molecules adsorbed. In other words, does the number of organized adsorbed molecules actually correspond in the three different experiments (at three different concentrations) to the actual number of molecules in solution? This can be checked three times, once for every concentration, each control being absolutely independent of the other, as the three dimensions are obtained from three different experiments. So that, should the figures coincide in every case, their correctness will have been proven three times independently.

*First control.*—Concentration  $1/750,000$ . The problem can be stated in the following way:—It is assumed that the horizontal space occupied by one single vertical molecule is

† R. A. Millikan, 'The Electron' (University Chicago Press, 1917).

$7.56 \times 6.64 = 50.2 \times 10^{-16}$  sq. cm. At a given dilution, namely  $1/750,000$ , it is assumed that they are all adsorbed on the free surface of the liquid + the surface of the glass. Consequently, as the total number of molecules present in the solution can be calculated (by dividing the mass of substance in solution by the mass of one molecule), the product—number of molecules  $\times$  area of one molecule—should be near the value of the total area of adsorption, namely  $26.41$  sq. cm.

We have in solution  $5.26 \times 10^{15}$  molecules; the area of a single molecule is  $50.2 \times 10^{-16}$ . The product is  $26.4$  sq. cm., identical with the surface of adsorption.

*Second control.*—Concentration  $1/1,220,000$ . Here we have, according to the same calculation,  $3.232 \times 10^{15}$  molecules in the solution. The space occupied by the tilted horizontal molecule is  $6.64 \times 12.30 = 81.7 \times 10^{-16}$  sq. cm. The product is

$$(81.7 \times 10^{-16}) \times (3.232 \times 10^{15}) = 26.4 \text{ sq. cm.}$$

*Third control.*—Concentration  $1/1,390,000$ . In this case the molecules lie flat, occupying an area  $7.56 \times 12.30 = 93.0 \times 10^{-16}$  sq. cm. We have  $2.838 \times 10^{15}$  molecules in solution. The product is

$$(93.0 \times 10^{-16}) \times (2.838 \times 10^{15}) = 26.4 \text{ sq. cm.}$$

In the three cases the figures check to the first decimal point.

It is not unnecessary to remark that there is no fallacy whatever in the foregoing reasoning. Each dimension is obtained from a separate set of experiments at a given dilution. This dimension—thickness of the layer of adsorbed molecules—is obtained from the known weight of substance present, assumed to be spread evenly on the total surface of adsorption. The thickness of two such layers (at two different critical concentrations) is then carried to the third experiment, and assumed to be the horizontal dimension of the individual molecule.

#### *Discussion and Evaluation of Errors.*

The errors involved in this method are small, because, with the exception of the determination of weights, volumes, and surface of adsorption, which can be performed with a

good degree of accuracy, no quantitative measurements of the surface tension are required. The whole computation depends on the determination of a minimum value of the surface tension of solutions after two hours' standing. Although these determinations require great care, they are remarkably constant, and the minima are sharply defined (Charts I., II., III., and Table I.).

If it be admitted that the molecular weight of sodium oleate is exact, or if we choose to neglect the possible error—which is certainly very small—in the atomic weights of its constituents, it may be stated that the error in the value of  $N$  is dependent solely on the errors involved in the determination of the mass of one single molecule of sodium oleate. This mass, as calculated from our measurements, may be expressed by the formula

$$M = \frac{m^3 \cdot C_1 \cdot C_2 \cdot C_3}{A^3 \cdot \delta^3}, \dots \dots \dots (1)$$

as one of the linear dimensions is equal to

$$L = \frac{m \cdot C}{A \cdot \delta}.$$

$M$  = mass of one molecule of substance (to be computed).

$m$  = mass of mixture in watch-glass, always assumed, at  $22^\circ \text{C.} = 2 \times 0.9979$  (temperature correction).  
This is true if density of water is  $1 \text{ gr./cm.}^3$ , and the concentration of the substance very small.

$A$  = area of adsorbing surface (total surface of water in contact with air and glass).

$\delta$  = specific gravity of substance in solution.

$C_1, C_2, C_3$  = critical concentrations at which the minima are observed.

The various values of the critical concentrations  $C_1, C_2$ , and  $C_3$ , corresponding to each of the three minima obtained from the various experiments, exhibited a degree of consistency which may be described by saying that the most extreme value, for any of these three points, has in no case differed from the mean of the values for that point by more than 0.2 per cent. It may be assumed that the error in the

determination of the area of the surface of adsorption does not exceed 0.2 per cent.

Since the determinations were made at constant temperature (22° C.) and with concentrations not greater than 1/750,000, or 0.000,001,333 gram per c.c. of water, it may be assumed safely that the error in the value of M used in the calculation is the same as the error in measuring the volume of the liquid used, which is not more than 0.1 per cent.

The possible error in M may be estimated, therefore, as follows:—

Factor.	Assumed error.
<i>m</i> .....	0.1 per cent.
C .....	0.2 „ „
A .....	0.2 „ „

and by reference to equation (1),

Factor.	Assumed error.
<i>m</i> <sup>3</sup> .....	0.3 per cent.
C <sub>1</sub> · C <sub>2</sub> · C <sub>3</sub> .....	0.6 „ „
A <sup>3</sup> .....	0.6 „ „
	<hr/> 1.5 per cent.

This error of 1.5 per cent. can occur only if all the several errors—nine in number—happen to have their maximum value and are of the *same sign*, which is obviously highly improbable. A calculation of the probable error, on the assumption that each of the individual errors has its maximum value but that it may be + or – with equal probability, gives the value 0.13 per cent. To this value must be added, of course with due respect to sign, twice the value of any error in the value of  $\delta$ . The various available values of  $\delta$  are identical, and expressed as accurate to within 0.1 per cent. (Beilstein).

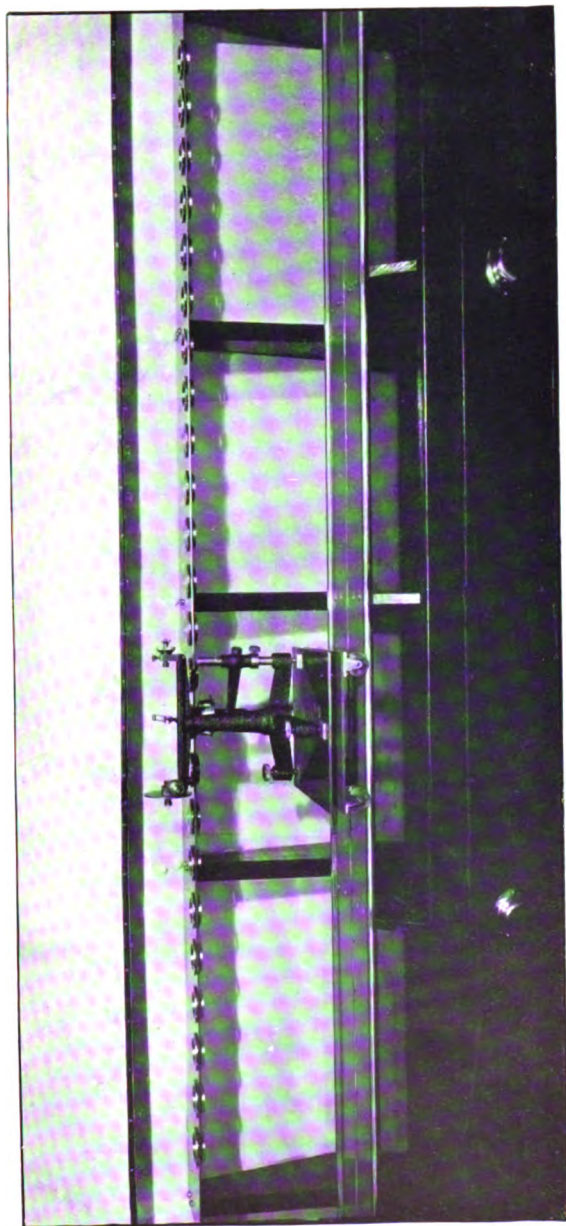
I believe, therefore, that the value of N calculated above is correct within 0.15 per cent., namely:

$$N = 6.003 \pm 0.08.$$

### *Discussion.*

Although the practical results of this experimental work are quite satisfactory as far as accuracy to the 2nd decimal point is concerned, and in spite of the good accord of the

calculated value of  $N$  with the most reliable figures thus far published, it must be kept in mind that the assumptions on which this work is based are open to discussion, and that the writer's interpretation of the experiments may be incorrect. This may not forcibly affect the numerical results, but it may simply increase, by a small amount, the value of the error. One may conceive, indeed, that the real interpretation of the facts, although totally different from a theoretical thermodynamic point of view, might nevertheless yield quantitative results which would be infinitely close to those derived from an approximate interpretation. For instance, it is impossible to admit, theoretically, that all molecules are adsorbed. They certainly are not; but the percentage of non-adsorbed molecules is relatively so small that it only introduces into the calculation an error of the order of magnitude of the experimental errors. The remarkable concurrence of the figures on pp. 668-669 between the measured surface of adsorption and the product (area of adsorbed surface of each molecule  $\times$  number of molecules in solution) appears to furnish a striking proof of the adsorption of all molecules. However, the figures check only to the first decimal place, which in itself is very remarkable, but allows an error of  $\pm 0.05$ , or 0.20 per cent. As the area of the adsorbing surface can only be measured within approximately  $\pm 0.2$  per cent., there is room for a certain number of free molecules in the solution. The assumption that all molecules are adsorbed is undoubtedly incorrect, but probably correct to the second or third decimal place. Suppose that instead of having  $26.6666 \times 10^{-7}$  gram contained in one watch-glass, adsorbed on the surfaces, which is our assumption, we had only  $26.6665 \times 10^{-7}$  gram, and that  $0.0001 \times 10^{-7}$  was in the solution. This would mean almost  $2 \times 10^{10}$  free non-adsorbed molecules. But since it amounts to only a difference of about 0.0004 per cent. in the weight in grams, it does not affect our calculation, nor does it affect the determination of the molecular dimensions, which are submitted to much larger experimental errors.



**SURFACE TENSION APPARATUS.**—The tensiometer (du Noüy) is seen rolling on a rigid carriage provided with an efficient brake. The solutions are on the upper table, in watch-glasses, and can be raised very smoothly. It is fundamentally important that the solutions suffer no jarring or jerking during the two hours elapsing before the last measurements are taken, nor when raised to meet the platinum ring by means of which the measurements are performed.





LXVIII. *Regularities in Band Spectra.* By SNEHAMOY DATTA, D.Sc. (London), M.Sc. (Calcutta), Professor of Physics, Presidency College, Calcutta\*.

[Plate XIV.]

1. *Introductory.*

THE analysis of band spectra into their component series has presented greater difficulty than the series classification of line spectra. In line spectra, the sorting out of the different series is facilitated by the experimental investigation of their Zeeman effect, pressure effect, and so forth, but such effects do not usually occur in band spectra. In the case of the less complicated band spectra, where there is an essential difference in the structure of the different groups, a classification can be made without any ambiguity; but in the absence of any such striking difference in the structure of the groups, it has been customary to select the series such that they conform with a particular type of formula. The formula which has been chiefly adopted for this purpose is one of the following type, originally proposed by Deslandres :

$$\nu = A + B[f'(m)]^2 + C[f'(p)]^2,$$

where  $m$  and  $p$  take successive integral values, usually large and not within any definite limit, the form of the function of  $m$  and  $p$  being varied so as to make the best fit. Recently, however, Heurlinger† and Lenz‡, following the line of treatment suggested by Bjerrum§ and Schwarzschild||, have developed a theory which has been successful in explaining many of the characteristics of band spectra. The theory has been very little¶ applied to explain the characteristics of the series of heads appearing in a group of bands. In the present paper, starting with the equation suggested by these authors, an attempt has been made to arrive at a general equation which may explain the different types of series found to exist among the band heads.

\* Communicated by the Author.

† Heurlinger, *Physik. Zeitschr.* xx. p. 188 (1919); *Zeitschr. f. Physik*, i. p. 82 (1920).

‡ Lenz, *Verhandl. d. Deutsch. Phys. Ges.* xxi. p. 632 (1919).

§ Bjerrum, *Nernst Festschrift*, p. 90 (1912).

|| Schwarzschild, *Berliner. Ber.* p. 548 (1916).

¶ Recently Kratzer (*Ann. der Physik*, lxvii. p. 127, 1922), also Sommerfeld (English translation), p. 434, has developed a theory for the explanation of series in the CN bands. His line of treatment is, however, entirely different.

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2. *Theoretical.*

According to Heurlinger and Lenz, the bands are produced by a simultaneous quantum change of the rotation of the molecules ( $M \rightarrow M'$ ), of the vibration of the atoms ( $p \rightarrow p'$ ), and of the electron system of the molecule ( $E \rightarrow E'$ ). The energy emitted by the molecule is the energy difference between the initial and final states in accordance with Bohr's frequency condition. These authors thus arrived at an equation of the type

$$\nu = \left[ \frac{W_{E'} - W_E}{p} \right] + [(a'p' + b'p'^2) - (ap + bp^2)] + [A'M'^2 - AM^2], \dots \quad (1)$$

where the first term within brackets represents the electron energy of the system, the middle one the energy of atomic vibration, and the last the energy of molecular rotation, in the final and initial conditions. The theory further maintains that the first two terms in equation (1) determine the characteristic frequency of a band (hence its position), whereas the quantum changes involved in the last term give its fine structure.

The system of discontinuous states corresponding to the quanta of atomic vibration is not stated, but it is possible to arrive at a physical interpretation in the following way. It is known from experiments which have nothing to do with spectra that a diatomic molecule can exist in at least two states which are discontinuously separated, namely the normal molecule and the normal atoms into which the molecule has dissociated. The other discontinuous states corresponding to the successive quantum changes must therefore be states of the molecule intermediate between these two states, or states of partial dissociation. And since for various reasons the atoms inside a molecule are regarded as linear oscillators—the vibration taking place along the line joining the nuclei—the partial dissociation will therefore be effected by the increase of the linear distance between the nuclei. Or in other words, the successive states correspond to the discontinuous increase in the linear distance between the nuclei. The atoms perform oscillations which are nearly but not quite harmonic, so that the energy in each state is given by

$$W_p = h(ap + bp^2),$$

where  $p$  refers to the numerical order of the successive states. With the change in the linear distance between the nuclei,

there will be a change in the position of the electron which serves as the connecting link between the atoms. Consequently, corresponding to each orbit\* of the atom it would be natural to expect one orbit of the link electron, the change from one orbit to another causing the radiation of the electron energy. But the approximate constancy of the first term in equation (1) seems to suggest that the electron has only two definite discontinuous states, possibly the bound and the free states, corresponding to the partially and completely dissociated states of the molecule.

The question of electron energy is, however, very obscure, and as it does not come within the scope of the present paper, it will not be further considered. In any case, the maximum of energy that can be radiated would correspond to a return of the atom from the limiting to its primary orbit.

Besides these two changes, there is another—viz., the energy of rotation of the molecule as a whole—which has to be taken into consideration. But the change of rotational energy involves only a very small change in the electron energy and in the vibrational energy† of the atoms which give rise to the head,‡ of a band. As the present paper deals with the regularities present among the band heads, the last term in equation (1) corresponding to the rotational

\* The orbits here referred to are the limited number of possible dissociated states of the molecule. The term has been used to maintain the analogy with the stationary electron orbits of Bohr.

† Kratzer has worked out this mutual action, and has represented it by  $-m^2 a_n h$ , where  $m$  is the rotational quantum and  $a_n$  is proportional to the oscillation quantum  $n$  (see 'Atomic Structure and Spectral Lines,' by Sommerfeld (English translation), p. 422). The shift due to the mutual action is therefore very small, and as the numerical relations in the band heads mainly involve the differences in wave-numbers between the bands having the same rotational quantum, the shift may be neglected altogether.

‡ More correctly speaking, the characteristic frequency  $\nu_0$ , which determines the position of the band. According to the theory of band spectra, the head of a band, as has been clearly pointed out by Curtis (Proc. Roy. Soc. A, ci. pp. 38-64), assumes only a secondary importance, it being a region where the lines happen to crowd together. The relation established in the present paper is therefore one to be expected among the characteristic frequencies  $\nu_0$  of each band. But owing to our want of knowledge of the structure of each band, it is not possible at present to seek for numerical relations amongst the characteristic frequencies of the bands. Curtis, however, has pointed out the definiteness of the relation between the apparent head of a band and its characteristic frequency [ $\nu = \nu_0 + h/8\pi^2(1-l')$ ]. As  $l, l'$  remain constant for the same system of bands, the numerical relations, which involve mainly the differences in wave-numbers, will be the same whether the frequency of the apparent head ( $\nu$ ) or the characteristic frequency ( $\nu_0$ ) are taken into consideration.

energy can be left out, so that equation (1) is modified to

$$\nu = \frac{W_{E'} - W_E}{h} + [(a'p' + b'p'^2) - (ap + bp^2)], \quad (2)$$

where  $p'$  and  $p$  refer to the initial and final orbits of the vibrating atoms. Had the oscillation been a purely harmonic one, the principle of correspondence would have required that  $p$  should never change by more than one unit. Consequently, though the oscillation is not strictly harmonic, but very nearly so, it is reasonable to suppose that the more probable changes are those that involve a change of one unit—i. e., the radiation takes place in a change from the  $p+1$  to the  $p$  orbit. Now in the ordinary condition the molecules are in different partially dissociated states—i. e., the atoms are in different orbits, the most probable orbit being a function of temperature. The final orbit  $p$  is therefore not the same for all molecules, but is of the form  $p = k + m$ , where  $k$  determines the minimum order number of the atom (i. e., corresponding to the shortest distance between the nuclei) and  $m$  takes all the ordinal values including zero. The general equation for such radiation will then be of the form

$$\begin{aligned} \nu &= \frac{W_{E'} - W_E}{h} + [\{a'(k+m+1) + b'(k+m+1)^2\} \\ &\quad - \{a(k+m) + b(k+m)^2\}] \\ &= \frac{W_{E'} - W_E}{h} + a' + b' + 2k \cdot b' + k(a' - a) + k^2(b' - b) \\ &\quad + m[(a' - a) + 2b' + 2k(b' - b)] + m^2(b' - b) \\ &= A + Bm + Cm^2, \quad \dots \dots \dots (3) \end{aligned}$$

where

$$B = (a' - a) + 2b' + 2k(b' - b) \quad \text{and} \quad C = (b' - b).$$

As  $b'$  is a small number and all other terms are differences of numbers of the same order of magnitude,  $B$  cannot be large and  $C$  must be exceedingly small. The characteristic of such a group of heads would be a close succession of heads with the intervals very slowly varying.

This class of bands is the most general one, and has been recognized before, this type of equation being previously used empirically to arrange into series various groups of bands\*.

\* The bands of alkaline earth fluorides have all been arranged into this form (see Proc. Roy. Soc. A, xcix. p. -).



spectra, so that there is a change from any orbit to any other orbit. The equations (3) and (4) could then be combined as

$$\begin{aligned} \nu &= \frac{W_{E'} - W_E}{h} [\{a'(k+m+n) + b'(k+m+n)^2\} \\ &\quad - \{a(k+m) + b(k+m)^2\}] \\ &= \frac{W_{E'} - W_E}{h} + k(a' - a) + k^2(b' - b) + m[(a' - a) + 2b'n \\ &\quad + 2k(b' - b)] + m^2(b' - b) + n(a' + 2b'k) + b'n^2 \\ &= A + m[D + 2b'n] + m^2C' + nB' + b'n^2, \quad \dots \dots (5) \\ &= A + mD + m^2C' + n(B' + 2b'm) + b'n^2, \quad \dots \dots (5a) \end{aligned}$$

where

$$\begin{aligned} A &= \frac{W_{E'} - W_E}{h} + k(a' - a) + k^2(b' - b), \\ D &= (a' - a) + 2k(b' - b), \\ C' &= (b' - b), \\ B' &= a' + 2b'k. \end{aligned}$$

The order of magnitude of  $B'$  will be that of  $B$  in (4)—*i. e.*,  $> 1000$ — $C'$  is a very small quantity and is of the order of  $C$  in (3),  $D$  is also of the same order as  $B$  in (3), and determines the change in the natural frequency of the atom due to the change of state. The characteristic of such heads will therefore be a succession of several groups of heads, the groups following at long intervals (order  $> 1000$ ), but the heads in each group—*i. e.*, the subheads—following at short intervals.

The equations (5) and (5a) are therefore the general equations which should represent the regularities in the band heads. They essentially differ from Deslandres' empirical formula in the numerical values of  $n$  and  $m$ , which are here simple integers, having definite physical meaning ( $m$  refers to the primary orbit of the atom, and  $n$  to change of quantum) unlike the arbitrary high integers used by Deslandres.

In the following sections a typical system of bands has been studied with a view to examining the applicability of the above equation.

#### *Regularities in the First Positive Bands of Nitrogen.*

The nitrogen bands of wave-lengths longer than  $\lambda$  5000, known as the first positive bands, consist of a number

(about 50) of similar sub-groups of bands. With moderate dispersion each sub-group is seen to be composed of several (usually five) bands degrading towards the violet. Regularities of separation appear amongst the corresponding heads of the successive 8 to 10 sub-groups. The interval then changes abruptly, and continues to be regular for the next 8 or 10 groups, and so on. Accordingly, the 8 or more of these sub-groups, capable of representation in series of the ordinary type, have been designated as a group. The entire set of first positive bands is thus composed of 5 and possibly 6 such groups, which are designated *a* to *f* respectively. The nomenclature has been adopted after Von der Helm \*, who suggested this to be the best method of grouping the bands (see III., Pl. XIV.).

A second arrangement of the bands was first suggested by Cuthbertson † and subsequently improved by Deslandres ‡ (see II., Pl. XIV.). In this arrangement the head of a band in one of the above sub-groups is related not to the corresponding head in the adjacent sub-groups, but to that of a sub-group in the adjacent group. The entire set has thus been represented by the formula

$$\nu = 22785 \cdot 1 - \frac{30 \cdot 319}{8} (2m)^2 + \frac{29 \cdot 363}{8} (2p+1)^2,$$

where *m* varies from 44 to 53, and *p* from 43 to 48.

In the present section, criticisms of the two existing arrangements have been attempted and a third arrangement proposed (see I., Pl. XIV.). This new arrangement, besides removing the existing defects, shows remarkable agreement with the theoretical formula previously discussed.

The defect of the Von der Helm arrangement lies in the grouping of the sub-groups. On the ground of numerical relations, it is essentially necessary that the spacing of the heads should be the same for all the sub-groups belonging to the same group. Out of this consideration, the data collected from the very exhaustive paper on the subject by Birge § clearly lead to the conclusion that the grouping ought to be different in some respects from that adopted by Von der Helm.

The data for the consideration of the grouping are given

\* Von der Helm, *Zeit. f. Wiss. Phot.* viii. p. 405 (1910).

† Cuthbertson, *Phil. Mag.* (6) iii. p. 348 (1902).

‡ Deslandres, *Comptes Rendus*, cxxxiv. p. 747 (1902).

§ Birge, *Astrophys. Journ.* xxxix. pp. 50-58 (1914).



in Table I. The first two columns show the previous denomination used by Birge after Von der Helm, and the one adopted in the present paper. The third and the fourth

TABLE I.

Sub-groups.					
Birge after Von der Helm.	Datta.	$\lambda$ . I. A.	$\nu$ .	Difference.	Remarks.
I $d_1$	I $c_2$	6788.614	14730.53		
IV $d_1$	IV $c_2$	758.054	797.12	66.59	
I $d_3$	I $c_3$	6704.735	14914.79		
IV $d_3$	IV $c_3$	674.908	981.48	66.69	
I $d_5$	I $c_4$	6623.574	15097.59		
IV $d_5$	IV $c_4$	594.418	164.34	66.75	
I $d_7$	I $c_5$	6544.881	15279.13		
IV $d_7$	IV $c_5$	16.403	345.90	66.77	
I $d_9$	I $c_6$	6468.597	15459.31		
IV $d_9$	IV $c_6$	40.768	526.10	66.79	
I $d_{11}$	I $c_7$	6394.628	15638.12		
IV $d_{11}$	IV $c_7$	67.416	704.96	66.84	
I $d_{13}$	I $c_8$	6322.816	15815.74		
IV $d_{13}$	IV $c_8$	296.212	882.57	66.83	
I $d_{15}$	I $c_9$	6252.806	15992.81		
IV $d_{15}$	IV $c_9$	26.978	6059.15	66.35	
I $d_{17}$	I $c_{10}$	6185.127	16167.82		
IV $d_{17}$	IV $c_{10}$	59.692	234.57	66.75	
<hr/>					
	I $d_0$	...	...	...	Not recorded.
I $e_1$	I $d_1$	6186.733	16163.62		
IV $e_1$	IV $d_1$	61.648	229.42	65.80	
I $e_2$	I $d_2$	6127.374	16320.20		
IV $e_2$	IV $d_2$	02.736	386.09	65.89	
I $e_3$	I $d_3$	6069.663	16475.38		
IV $e_3$	IV $d_3$	45.484	541.27	65.89	
I $e_4$	I $d_4$	6013.575	16629.04		
IV $e_4$	IV $d_4$	5989.812	694.73	65.69	
I $e_5$	I $d_5$	5959.053	16781.19		
IV $e_5$	IV $d_5$	35.740	847.10	65.91	
I $e_6$	I $d_6$	5906.010	16931.90		
IV $e_6$	IV $d_6$	883.146	997.70	65.80	
I $e_7$	I $d_7$	5854.404	17081.16		
IV $e_7$	IV $d_7$	32.054	146.62	65.46	
I $e_8$	I $d_8$	5804.435	17229.10		
IV $e_8$	IV $d_8$	782.059	294.87	65.77	
I $e_9$	I $d_9$	5755.188	17375.62		
IV $e_9$	IV $d_9$	35.555	441.19	65.57	
I $e_{10}$	I $d'_{11}$	5707.580	17520.56		
IV $e_{10}$	IV $d'_{11}$	685.199	589.53	68.97	
I $e_{11}$	I $d'_{12}$	5660.842	17665.22		
IV $e_{11}$	IV $d'_{12}$	38.868	734.06	68.84	
I $e_{12}$	I $d'_{13}$	5615.318	17808.43		
IV $e_{12}$	IV $d'_{13}$	...	...	...	No data.

Sub-groups.

Table I. (continued).

Birge.	Datta.	$\lambda$ . I.A.	$\nu$ .	Difference.	Remarks.
I $e_{13}$	I $d'_{14}$	5570.777	17950.82	24.31 } *	
II $e_{13}$	II $d'_{14}$	63.244	975.13		
I $e_{14}$	I $d'_{15}$	5527.150	18092.55		
II $e_{14}$	II $d'_{15}$	19.682	116.98		
I $e_{15}$	I $d'_{16}$	5584.338	18233.75	24.43 }	
II $e_{15}$	II $d'_{16}$	...	...		
		...	...	...	No data.
	I $e_0$	...	...	...	Not recorded.
I $f_1$	I $e_1$	5632.75	17753.32	...	No data.
IV $f_1$	IV $e_1$	...	...		
I $f_2$	I $e_2$	5592.881	17879.87	65.89	
IV $f_2$	IV $e_2$	72.347	945.76		
I $f_3$	I $e_3$	5553.730	18005.91	65.83	
IV $f_3$	IV $e_3$	33.504	071.74		
I $f_4$	I $e_4$	5515.594	18130.40	65.41	
IV $f_4$	IV $e_4$	95.763	95.81		
I $f_5$	I $e_5$	5478.471	18253.27	65.50	
IV $f_5$	IV $e_5$	58.879	318.77		
I $f_6$	I $e_6$	5442.325	18374.50	65.45	
IV $f_6$	IV $e_6$	23.014	439.95		
I $f_7$	I $e_7$	5407.129	18494.10	65.36	
IV $f_7$	IV $e_7$	388.087	559.46		
I $f_8$	I $e_8$	5372.820	18612.20	65.44	
IV $f_8$	IV $e_8$	53.992	677.64		
I $f_9$	I $e'_1$	5339.432	18728.59	57.87	
IV $f_9$	IV $e'_1$	22.983	86.46		
I $f_{10}$	I $e'_2$	5306.859	18843.53	...	No data.
IV $f_{10}$	...	...	...		
I $f_{11}$	I $e'_3$	5275.072	18957.10	...	No data.
IV $f_{11}$	IV $e'_3$	...	...		
I $f_{12}$	I $e'_4$	5244.071	19069.16	...	No data.
IV $f_{12}$	IV $e'_4$	...	...		
I $f_{13}$	I $e'_5$	5213.808	19179.84	64.36	
IV $f_{13}$	IV $e'_5$	196.370	244.20		
I $f_{14}$	I $e'_6$	5184.237	19289.24	64.13	
IV $f_{14}$	IV $e'_6$	67.060	353.37		
I $f_{15}$	I $e'_7$	5155.323	19397.42	...	No data.
IV $f_{15}$	...	...	...		
I $f_{16}$	I $e'_8$	5126.806	19505.11	...	No data.
IV $f_{16}$	...	...	...		

\* The fourth band is not recorded; but the difference between the first and second band in each sub-group shows that they belong to the same series.

columns give the wave-lengths and wave-numbers of the first and fourth band in each sub-group, the second, third, and the fifth being omitted for the sake of brevity. The fifth column gives the difference in wave-numbers of the two bands. When the head has not been definitely marked out by Birge, the strongest line on the red side has been taken as the head.

The fifth column of Table I., which gives the interval between the heads, clearly indicates that, using the old nomenclature, all the sub-groups from  $d_4$  to  $d_{12}$  belong to the same series. The name of the series has been changed from  $d$  to  $c$ , because according to the new classification all the sub-groups on the less refrangible side are clustered into two groups ( $a, b$ ), and not into three groups ( $a, b, c$ ) as previously suggested by Von der Helm.

The numbering of each sub-group has to be changed also, but the previous idea of counting the sub-groups from the long wave-length side has been adopted.

Referring back to column 5 (Table I.) and using the old nomenclature, the spacing of the heads appears to remain nearly constant up to  $e_9$ , after which it suddenly changes, but remains constant for the next two members. From  $e_{12}$  to  $e_{13}$  the data are insufficient to show whether these latter members belong to the same series as  $e_{10}$  and  $e_{11}$ . In any case, the regular series consists of the sub-groups  $e_1$  to  $e_9$ , and they have been re-named as  $d_0$  to  $d_8$  in accordance with the nomenclature adopted for the preceding series. For reasons which will be mentioned later, the remaining sub-groups are regarded as belonging to a different system ( $d'$ ) having no apparent relation with the one which forms the regular series. Following the same analysis, the sub-groups  $f_1$  to  $f_8$  are regarded as the regular series, whereas the later members from  $f_9$  to  $f_{15}$  are excluded; they perhaps belong to the previous irregular system.

Fresh support in favour of the revision of groupings as suggested in this paper has been obtained from an examination of the intensity of the sub-groups. In both the old  $e$  and  $f$  groups, the intensity of the sub-groups suddenly diminishes after  $e_9$  and  $f_8$ —that is, exactly where the divisions have been made. The old  $f$  group presents two distinct maxima—one at  $f_5$  and the other at  $f_{12}$ . In the  $e$  group also, besides the first maximum at  $e_6$  there is an indication\* of a second maximum at  $e_{13}$ .

The presence of two maxima in the same series is contrary to our existing knowledge of band spectra. According to the grouping adopted here, there is only one sub-group showing the maximum of intensity, and this is roughly in the middle of each group.

Further evidence in justification of the above mode of division is obtained by examining the structure of the bands constituting each sub-group. In the first heads of

\* This is not very pronounced owing to the overlapping of some of the  $f$  sub-groups.

the members of the  $f$  group there appears an extremely heavy doublet. Birge, from consideration of (1) the spacing of this doublet and (2) the numerical relation of the series, has suggested that "the group consists really of two groups." Although Birge did not record any such doublet in the first heads of the members of the  $e$  group, the existence of a second line on the more refrangible side of the first head has been traced in all the sub-groups. The differences in wave-numbers of these two lines for the entire sub-groups of the old  $e$  group are:—

	$e_{1.}$	$e_{2.}$	$e_{3.}$	$e_{4.}$	$e_{5.}$	$e_{6.}$	$e_{7.}$	$e_{8.}$
Diff. in wave-numbers ...	1.14	1.15	1.04	1.05	1.12	1.0	1.08	1.06

	$e_{9.}$	$e_{10.}$	$e_{11.}$	$e_{12.}$	$e_{13.}$	$e_{14.}$	$e_{15.}$
Diff. in wave-numbers ..	1.0	0.96	0.41	0.42	0.50	0.41	0.38

The spacing of the two lines thus continues to be very nearly constant up to  $e_9$ ; it then changes, and again remains roughly constant up to the end of the group, suggesting that the  $e$  group likewise consists of two groups.

Thus from various considerations of numerical relationships and otherwise, the mode of grouping suggested in this paper seems to be most significant. And this form of arrangement being essentially similar to that of Von der Helm, has all the advantages over the Cuthbertson arrangement already pointed out by Birge, viz.:—"It is possible to fit a greater number of lines into the simple series of the Von der Helm arrangement of bands than into the more complex two-parameter formula indicated by the Cuthbertson arrangement."

In the second form of arrangement proposed by Cuthbertson a band in one of the sub-groups is related, not to the corresponding band in the adjacent sub-group, but to that of a sub-group in the adjacent group. Thus, according to his arrangement, there are as many vertical series as the maximum number of sub-groups in a group, so that the vertical series are the same as adapted here. The horizontal series, however, instead of representing the relation between all the sub-groups in a group (as the present arrangement does), are picked out in the way which best fits in with the empirical formula quoted before. The horizontal series in his arrangement consists of members which fall on lines parallel to the diagonal drawn in Table II.

It is a very important condition for the fulfilment of series-relations that the spacing of the bands must be the same for the sub-groups constituting one series. The spacing

of the bands has been calculated in Table I. (column 5) for the four groups, *c*, *d*, *e*, and *f*. It is therefore clear that in Cuthbertson's arrangement, neither the sub-groups forming the horizontal series nor those forming the vertical series have the same spacing. In the present arrangement the sub-groups in a horizontal series have very nearly the same spacing, but those in a vertical series have slightly different spacing, the difference being an actual one, and not due to any error of measurement. An explanation is given in the following way. Why each sub-group has so many bands (under small dispersion three) is not completely understood. In connexion with the iodine fluorescent bands, it has been suggested \* that some change in rotational energy causes the displacement of the band heads. The same thing might be happening with nitrogen. The change in rotational energy may be caused by a change in the moment of inertia of the molecule. The moment of inertia of a diatomic molecule can be calculated by assuming the masses  $m_1$  and  $m_2$  of the atoms concentrated at the nuclei. If they are at a distance  $l$  apart, then

$$I = \frac{m_1 m_2}{m_1 + m_2} l^2.$$

According to what has been put forward in the theoretical section, the different orbits of the atoms correspond to different distances between the nuclei; consequently,  $I$  should be different for different orbits. A change in  $I$  corresponds to a change in  $l$ , and is therefore likely to be very nearly the same for the same quantum change but different for different quantum changes. Now, the bands in the horizontal series, according to the present scheme, refer to the same quantum change, whereas those in vertical series correspond to different quantum changes; consequently, the same spacing in the horizontal series and different spacing in the vertical series are what we should expect.

On the other hand, a change in physical condition of the source has been suggested as an indication that the Cuthbertson arrangement may be more significant. Fowler and Strutt † have shown that the spectrum of the active modification of nitrogen shows certain of the sub-groups of the 1st positive bands greatly intensified, while the others are very faint. Those intensified formed three successive horizontal rows according to Cuthbertson's arrangement, whereas they had no apparent significance according to that of Von der Helm. But according to the present arrangement they

\* W. Lenz, *Phys. Zeit.* xxi. p. 691 (1920); Kratzer, *Zeit. für Physik*, (3), v. p. 289 (1920).

† Fowler & Strutt, *Proc. Roy. Soc.* lxxxv. p. 377 (1911).

are the last three members in the horizontal series. So that it may be inferred that the nature of the stimulus in the afterglow is such as to develop the higher members of a series. The enormous concentration of energy at the end of the afterglow CN bands also supports this view. In a separate section the nature of the afterglow spectrum will be discussed in the light of the present theory.

Another change in physical condition is to be noticed in the experiments of Angerer\*, who made a comparative study of these bands at the ordinary temperature and that of liquid air. The main results of his experiments are that at low temperature all the sub-groups are weak, sometimes only the first band in each sub-group appearing; but some of the sub-groups comparatively retain their intensity, and thereby appear to be stronger than the others. Generally speaking, these are either the stronger members of the sub-groups appearing under the ordinary condition of discharge, or the earlier numbers of these sub-groups which have been left out of the regular groups, *d*, *e*, etc., and have been recognized as forming altogether different groups, named as the *d'* and *e'* groups. As belonging to the first class may be mentioned the bands at  $\lambda 6623\cdot5$  (new *c*<sub>3</sub>),  $\lambda 6069\cdot6$  (new *d*<sub>2</sub>) and  $\lambda 5478\cdot4$ ,  $\lambda 5442\cdot3$ ,  $\lambda 5407\cdot1$ ,  $\lambda 5372\cdot8$  (new *e*<sub>1</sub>, *e*<sub>2</sub>, *e*<sub>3</sub>, and *e*<sub>7</sub>). Whereas the bands at  $\lambda 5615\cdot3$ ,  $\lambda 5570\cdot7$  (new *d'*<sub>3</sub> and *d'*<sub>1</sub>),  $\lambda 5339$ ,  $\lambda 5306$  (new *e'*<sub>1</sub> and *e'*<sub>2</sub>) belong to the second class. These latter bands are also those which are very weak at ordinary temperature. Roughly speaking, therefore, the groups whose regularities have been definitely established consist of sub-groups which are stronger under the ordinary condition of the discharge-tube but weaker at low temperatures; whereas those groups (named with dashes) whose regularities are not so definitely shown on account of the insufficiency of their number, consist of sub-groups which are weak under ordinary circumstances and comparatively strong at low temperature. The behaviour at low temperature is hardly explicable by either of the Von der Helm or Cuthbertson arrangements, but the present arrangement explains it in a very significant way.

Eliminating † in this way a few of the sub-groups, for the various reasons pointed out above, those remaining have been

\* Angerer, *Ann. der Phys.* xxxii. p. 549 (1910).

† It must be made sufficiently clear that even if these sub-groups be included in the corresponding group, the scheme of arrangement suggested in the paper stands. Only the *m*—the quantum number of the successive orbits—has to be increased (see Table II.) This would then indicate that at ordinary temperature the stimulus creates some more unstable orbits than are expressed in Table II., but at lower temperatures the higher members are suppressed.

arranged as shown in Table II. The successive integral values of  $m$  on a horizontal line refer to the successive orbits of the atoms in falling back to where the radiation is supposed to occur; the corresponding values of  $n$ , written in brackets, determine the change of number of orbits (quantum changes) involved in the fall. Thus the first number in group  $a$  is due to a fall from the 1st quantum orbit to the 0th one, the second to a fall from the 2nd orbit to the 1st, and so on. Similarly, in group  $f$ , the first is due to a fall from the 2nd quantum orbit to the 0th one, the second for a fall from the 3rd orbit to the 1st, and so on.

In Table II. the observed wave-lengths and the calculated wave-numbers of the first heads of each sub-group are collected, and the difference in wave-numbers between the successive sub-groups are shown at the top. Each horizontal row thus represents a series of the usual type, expressible by an equation :

$$\nu = A + Bm + c'm^2.$$

Proceeding from one series to another, the differences between the corresponding adjacent sub-groups—roughly expressed by the constant  $B$ —gradually decrease by a constant amount. Taking the  $m=0$ th member of each series as its head, the relation between the different heads may be conveniently expressed as shown in Table III.

TABLE III.

Series $n$ .	$\nu$ .	$\delta\nu$ .	$d(\delta\nu)=2b'$ .	$\Delta\nu=B$ .	$d(\Delta\nu)$ .
0 .....	9244.8	1733.7			
1 .....	10978.5	1704.7	29.0	245.0	29.0
2 .....	12683.2	1675.7	29.0	216.0	29.0
3 .....	14358.9	1646.7	29.0	187.0	29.0
4 .....	16005.6	1617.7	29.0	158.0	29.0
5 .....	17623.3	1588.7	29.0	129.0	29.0
6 .....	19212.0			100.0	

The vertical series, given in the second column of the above table, is also of the ordinary type expressible in the form :

$$\nu = A + B'n + b'n^2.$$

[To face page 686.]

ogen.

9.	10.	11.	12.	Remarks.
—	—	—	—	Measures from Coblentz, probable error 0.1 $\mu$ .
133.1	232.4	231.0	229.6	Measures from Croze, probable error "several angstroms."
—	13365.5	13396.5	13826.1	—
—	—	—	—	—
574.0	202.6	201.5	—	Measures from Birge taken on the Hilger spectroscope, probable error 1 A.
—	14776.6	14978.1	—	—
—	—	—	—	—
552.81	6185.13	—	—	Measures from Birge, probable error 0.02 A.
991.34	174.38	16165.72	—	—
1.47	2.09	—	—	—
755.19	—	—	—	Do.
375.66	—	—	—	Do.
-0.04	—	—	—	Do.
—	—	—	—	Do.
—	—	—	—	† Measures from Angstrom & Thalen. * Visually observed by Fowler & Strutt.









Combining the two, the general equation is of the form :

$$\nu = A + Bm + c'm^2 + B'n + b'n^2,$$

$n$  remaining constant, variations of  $m$  give the horizontal series, and  $m$  remaining constant, variation of  $n$  gives the vertical series. The coefficient  $B$  changes from one horizontal series to another by a constant multiple, as shown in columns 5 and 6 of the preceding table.  $B$  is therefore of the form  $B = D + 2b'n$ , where  $D$  is a constant. The general equation is thus reduced to

$$\nu = A + m(D + 2b'n) + c'm^2 + B'n + b'n^2,$$

a form identical with the theoretically deduced equation (5). An approximate solution of the general equation can be given by

$$\begin{aligned} \nu = 9244.8 + m(274.75 - 29.0n) + (-0.75)m^2 \\ + 1748.2n + (-14.5)n^2. \end{aligned}$$

The values of the various constants are of the same order as predicted by the theoretical equation.

In the arrangement shown in Table II. it has been assumed that the stimulus creates comparatively unstable orbits up to 13, and that radiation takes place in the fall from these unstable orbits to those of comparatively greater stability by change of 1, 2, or more quanta. Thus, as one proceeds downwards, the groups corresponding to higher quantum changes must have one sub-group less than the previous one. Thus the group  $e$ , with a quantum change of 5, cannot have any sub-group beyond the one corresponding to the 8th orbit, and so on. At the same time the group with zero quantum change cannot have more than one sub-group; for the absence of a quantum change means the absence of the atomic vibration; consequently the only radiation possible is that due to a change of the electron energy. As this may involve a change of the rotational energy of the molecule as a whole, the total radiation would correspond to that of only one sub-group with its first head at  $1.08\mu$ , as calculated by an interpolation of the data shown in column 2 of Table II. Arranging the sub-groups empirically, a glance at Table II. would indicate that there should be a succession of sub-groups in the first horizontal row instead of the single one as predicted by the theory. (Coblentz \*, from the infra-red measurements of the emission

\* W. W. Coblentz, Publication No. 35, Carnegie Institution of Washington.

spectra of vacuum tubes, has recorded a sharp maximum at  $1.06\mu$ . The sharpness of the maximum would indicate the presence of a single band, thus proving the validity of the above suggestion.

With regard to the other groups having quantum changes 1, 2, etc., Table II. shows that all the calculated members have not been actually observed. Peculiarly, however, with small quantum changes the bands corresponding to the higher orbits are missing, and with higher quantum changes those corresponding to the lower orbits are missing. Most of these missing bands overlap with those of the groups either preceding or following their own, and so it may be that their presence is masked by the others. It is possible, however, to explain their absence in the light of the present theory in a different way.

Each band involves a change between two orbits, one unstable and the other comparatively stable. According to the nature of the stimulus a molecule receives, the constituent atoms are raised to different unstable orbits. If a molecule receives high stimulus, a greater number of unstable orbits are created, and at the same time its stable orbits correspond to partially dissociated states of higher order. If it receives low stimulus, the higher members of the unstable orbits are not at all formed, and the stable orbits correspond to dissociated states of lower order.

Consequently, for higher quantum changes (higher stimulus) bands corresponding to lower orbits (*i. e.*, less dissociated states) are not observed, and for lower quantum changes (less stimulus) bands corresponding to higher orbits (*i. e.*, more dissociated states) are also not observed. In the discharge-tube, even under ordinary conditions, different molecules receive different degrees of stimulus, and that is why we find so many groups corresponding to lower as well as higher quantum changes. With the gradual increase of stimulus in the discharge, it is evident that molecules in the higher states of dissociation will be more numerous; consequently the intensity distribution in groups of higher values of  $n$  (quantum change) will have its maximum moving towards higher values of  $m$  (higher dissociated states). No actual experiment is on record to test this view, but the general distribution of intensity in the successive groups under ordinary conditions of discharge roughly points to the same conclusion. In fig. 1 (Pl. XIV.) the maximum of intensity for the *c* group corresponds to  $m=5$  ( $\lambda 6544.89$ ), for the *d* group at  $m=7$  ( $\lambda 5854.40$ ), and for the *e* group at  $m=8$  ( $\lambda 5372.82$ ).

The groups corresponding to quantum changes of 7 and upwards have not been collected in Table II. They overlap with the second positive bands, which are far stronger. Besides, owing to high stimulus, molecules cannot be expected to remain in the lower states; consequently, under favourable condition only, the bands corresponding to the last one or two members may be expected in each group.

*The Significance of the Afterglow Bands.*

In the same way it is possible to understand the characteristic of the afterglow spectrum. Owing to the enormous concentration of energy in the development of the afterglow bands, the stable states of the molecules correspond to the higher dissociated states. Consequently, only the bands corresponding to these higher states alone are greatly intensified. Those corresponding to the lower states are either missing altogether or appearing in greatly reduced intensity. In all cases where the bands are developed in the afterglow this feature is very prominent.

In some cases, still higher dissociated states and a greater number of unstable orbits are created, with the consequent development of a larger number of bands towards the tail. The group of heads forming the CN band at  $\lambda 4216$  has been roughly arranged in series by the equation :

$$\nu = \nu_0 + 116m - 8m^2.$$

The values of the coefficients of  $m$  and  $m^2$  having opposite signs, the series turn back after certain values of  $m$  ( $m=7$ ), with the result that there is a crowding of several heads (about 7) in the small region between  $\lambda 4143$  and  $\lambda 4153$ . Assuming, as has been suggested above, that a greater number of heads appear in the afterglow spectrum than in the ordinary arc, one would expect a crowding of lines at the tail. The cyanogen bands developed by acetylene in the afterglow of active nitrogen by Fowler and Strutt\* fully confirm this view.

*Infra-red Absorption corresponding to the Emission of the First Positive Bands.*

In the theoretical section, in connexion with equation (5) it has been mentioned that the value of the coefficient  $B'$  is of the same order of magnitude as  $a'$ , the natural frequency of vibration of the atom, and that  $D$  approximately determines

\* A. Fowler and R. J. Strutt, Proc. Roy. Soc. A, lxxxvi. (1912).  
*Phil. Mag.* S. 6. Vol. 48. No. 286. Oct. 1924. 3 A

the change in  $a'$  due to a change in the quantum states. The positive value of  $D$ , as obtained in equation (6), therefore suggests that the natural frequencies in the higher dissociated states are gradually decreasing numbers, the frequency in the state order number  $m$  being expressed as  $B' - mD$ . As the atoms are expected to absorb most readily the waves which correspond to their own natural frequency, the waves corresponding to the numbers  $B' - mD$  will be strongly absorbed. Besides these there will be a comparatively weaker absorption of the waves corresponding to the upper harmonics of the free vibrations of the atoms in the different states. Consequently the general equation, giving the absorption in the infra red, will be of the form  $n(B' - mD)$ ,  $m$  and  $n$  having successive integral values.

The absorption bands of nitrogen in the infra red are not on record, but Coblenz\* has made a study of the infra-red emission from discharge-tubes containing nitrogen. Besides the sharp maximum at  $1.06\mu$  mentioned before, he observed noticeable deflexions in the region between  $4.8$  to  $6.5\mu$ , without any sharp maximum anywhere. This would therefore correspond to a series of radiations with small differences in their frequencies. The calculated frequency corresponding to  $B'$  in equation (6) is  $5.73\mu$ . The emission corresponding to the vibrations of the atoms in the different dissociated states, given by the equation  $B' - mD$ , therefore closely agrees with those described by Coblenz. It would, however, be very interesting to test whether the absorption bands of nitrogen are actually found in this region or not.

#### *Correlation with the Ionization Potential Experiments in Nitrogen.*

It has been suggested in the theoretical section that corresponding to the successive higher values of  $m$  the molecule is in gradually higher states of dissociation, so that the maximum of energy that can be radiated would correspond to a return of the atom from the limiting orbit to its primary orbit (i. e.,  $m=0$ ). Owing to the superposition of the bands of the second group, and also owing to the experimental difficulties attended with the production of such higher orbits, the corresponding radiation has not been recorded. But it is possible to calculate it indirectly. The bands in the first column are seen to slowly converge; clearly the maximum radiation would correspond to the convergence

\* *Loc. cit.*

frequency. Since the heads of the groups may be calculated by the equation

$$\nu = 9244.8 + 1748.2n - 14.5n^2,$$

$\nu$  is maximum, given by  $\frac{\partial \nu}{\partial n} = 0$ ; i. e., for  $n = \frac{1748.2}{2 \times 14.5} = 60$ .

Thus  $\nu_{\max} = 61936.8$ , which corresponds to the energy acquired by an electron falling through a potential difference  $V$ , where  $V$  in volts is given by the quantum relation

$$\frac{eV}{300} = h\nu; \therefore V = 7.6 \text{ volts.}$$

By the ionization potential experiments of Franck and Hertz, Brandt\*, experimenting with nitrogen, has recorded a number of notches in his photo-electric curve which, when converted to the wave-length scale, correspond to bands identical in structure with the first positive bands of nitrogen. The potential corresponding to this ionization is 7.9 volts. It is clear that the ionization current cannot be due to the liberation of electrons by a complete dissociation of the molecules, for this would entail the ionization of at least one of the constituent atoms, which for nitrogen atom is much higher. It is, however, likely that the photo-electric currents are due to the ionization of the nitrogen by the ultra-violet radiation of the extended series of the first positive bands corresponding to the limiting orbits. The remarkably close agreement with the calculated value indicates that there may be some truth in the above suggestion.

The cases of other complicated bands—for example, the second positive bands of nitrogen, the negative bands of nitrogen, and the red cyanogen bands—have also been studied. They all show satisfactory agreement with the formula deduced.

#### SUMMARY.

1. On the basis of Heurlinger and Lenz's equation for the band spectra, three different equations have been obtained which may express the relation between the characteristic frequencies in a system of bands.

2. The case of the most complicated system has been studied in detail with reference to the first positive bands of nitrogen. Their series equation has been obtained, and it

\* Brandt, *Berliner dissertation*. See Franck, *Phys. Zeit.* xxii. pp. 388, 409, 441, 466 (1921).



shows perfect similarity with the equation theoretically deduced.

3. The significance of the afterglow bands has been discussed in the light of the theory.

4. From the data available from a study of the emission bands, the character of the infra-red absorption bands has been discussed.

5. A possible method of correlation with the ionization potential experiments in nitrogen has been suggested.

#### DESCRIPTION OF THE PLATE.

First positive bands of Nitrogen.

- I. Scheme adopted in the present paper.
- II.   "       "       by Cuthbertson.
- III.   "       "       " Von der Helm.

#### LXIX. *Some Problems of Two-Dimensional Electrostatics.*

By D. M. WRINCH, *D.Sc.*, *Lecturer at Lady Margaret Hall, Oxford* \*.

##### SUMMARY.

THIS paper treats electrical problems relating to infinite cylindrical conductors whose curves of cross-section are of the form

$$\left. \begin{aligned} x &= na \cos t + b \cos nt \\ y &= na \sin t - b \sin nt \end{aligned} \right\}, \dots \dots (1)$$

with  $n$  any positive integer and  $b$  not greater than  $a$ . This class of curves depending on three parameters  $a$ ,  $b$ , and  $n$  is of considerable generality and comprises the closed nodeless epicycloids of retrograde type sometimes also called hypotrochoids, which are among the curves traced out by a point whose motion is compounded of two uniform circular motions in opposite senses. They exhibit the phenomena of convexities and concavities and outward pointing cusps.

By means of the complex variable  $w$ , defined by the relation

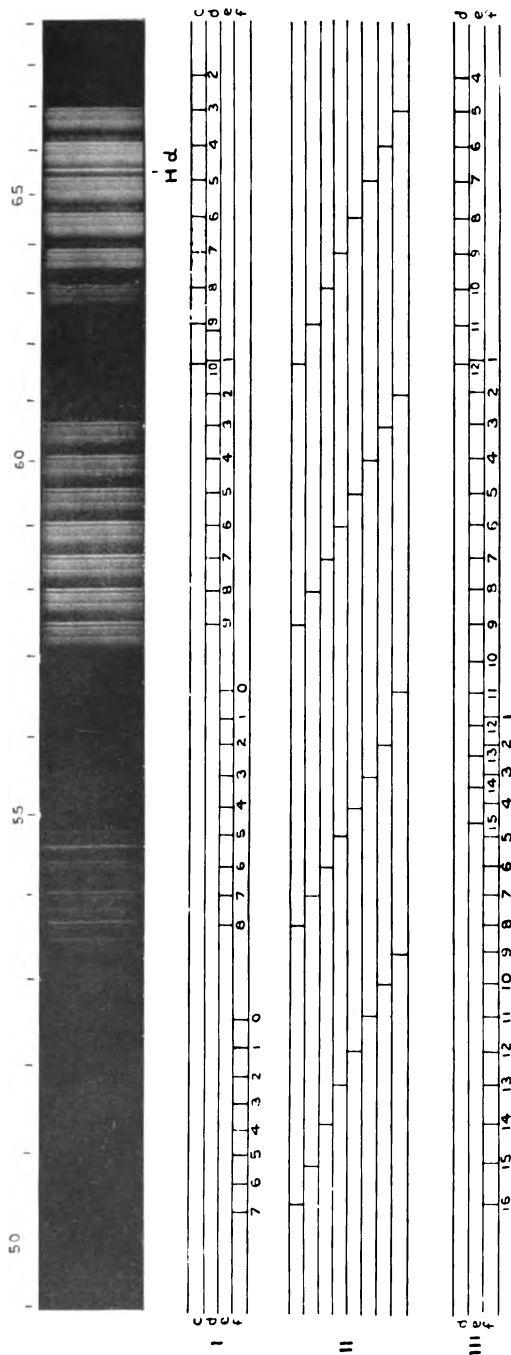
$$z = na e^{inw} + b e^{-nw},$$

the problem of a freely charged cylinder of type (1) is solved and the surface density of electrification at any point of the cylinder specified by the parameter  $t$  or the radius vector  $r$  is given by

$$\begin{aligned} 4\pi\sigma &= 2e \left| \frac{ds}{dt} \right| \\ &= 2e/n(a^2 + b^2 - 2ab \cos(n+1)t)^{\frac{1}{2}} \\ &= 2e/n^{\frac{1}{2}}(n+1)(na^2 + b^2 - r^2)^{\frac{1}{2}} \end{aligned}$$

if  $e$  is the charge on the cylinder per unit length. This result in the

\* Communicated by the Author.





special cases when  $a$  and  $b$  are equal and the curve of cross-section is cusped is exhibited also in the form

$$4\pi\sigma = (n-1)e/np,$$

where  $p$  is the perpendicular from the centre on the tangent to the curve of cross-section at the point. It presents an interesting contrast to the result for the cylinder of elliptic cross-section

$$4\pi\sigma = 2ep/(a^2 - b^2).$$

In the course of this investigation, it is found that all the hypotrochoids  $(a, b)$  of any specific positive integral order  $n$ , for which  $a^n b$  has a constant value, form a set of equipotentials, in the sense that if the cylinder whose cross-section is any one of them is freely electrified, the equipotentials are the cylinders external to it whose cross-sections are the other members of this set. This result provides a wide generalization of the equipotential character of sets of confocal ellipses. This fact allows the solution of the problem of the condenser formed by two cylinders  $(a_1 b_1 n)$   $(a_2 b_2 n)$  of type (1) in the case when  $a_1^n b_1 = a_2^n b_2$ . Its capacity is found to be

$$1/(2 \log (a_2/a_1))$$

per unit length.

An investigation is also included of the electrification of a cylinder of type (1) when insulated in a uniform field of electric force. If the strength of the field is  $f$  and if the lines of force in the undisturbed field make an angle  $\alpha$  with the axis of  $x$ , the surface density is given by

$$4\pi\sigma = 2fa \cos (t - \alpha) / (a^2 + b^2 - 2ab \cos (n+1)t)^{1/2}.$$

### Introduction.

**T**HE problem of the electrification of cylindrical conductors of infinite length has been solved in a variety of cases. In each case the fundamental problem is the electrification when the conductor is freely charged. When this has been solved it is in general possible to treat the conductor placed in any electric field, whether the field is expressed as a general law—as, for example, the uniform field—or as the effect of a system of discrete line charges or doublets outside the conductor.

The solution of two-dimensional electrostatic problems has so far been accomplished mainly by the use of the principle of conformal transformation. This method has permitted the solution of a few simple cases, notably the case when the curve of cross-section of the cylinder is an ellipse or a hyperbola, and of a wide variety of isolated cases when the curve of cross-section is, for example, a rectangle or a circular arc or an equilateral triangle. The solution when the curve of cross-section is an ellipse or a hyperbola is of fundamental importance on account of the fact that the equipotentials associated with an elliptic or hyperbolic

cylinder when it is freely charged are the elliptic or hyperbolic cylinders confocal with it and external to it. The solution in this case, in fact, shows that a family of confocal ellipses—and equally a family of confocal hyperbolæ—forms a set of equipotentials in the sense that a freely charged cylinder whose curve of cross-section is any member of the family has as its equipotentials the cylinders external to it, whose curves of cross-section are the other members of the family. And the great importance of the solution of the elliptic and hyperbolic cylinders is, indeed, due to the fact that the equipotential set to which an ellipse belongs is the family of confocal ellipses, and that the equipotential set to which a hyperbola belongs is the family of confocal hyperbolæ.

It has therefore been deemed worth while to call attention, in this paper, to certain families of simple curves which form sets of equipotentials and to submit the solution of the fundamental problem of the corresponding cylinders when they are freely charged and of the most important of the subsidiary problems, the problem of the induction in a uniform field of force. Certain types of condensers are also considered.

The curves are of algebraic type and include the ellipse and hyperbola as a special case. We refer to the closed nodeless epicycloids of integral order  $n$  of retrograde type, defined in terms of a parameter in the form

$$\begin{aligned}x &= na \cos t + b \cos nt, \\y &= na \sin t - b \sin nt,\end{aligned}\quad (b \leq a)$$

where the product  $a^n b$  is constant, and to their orthogonal trajectories. These epicycloids are easily visualized as the paths of points whose motion is compounded of two uniform circular motions. They also present themselves in another manner as the path traced out by a point on a circle which rolls in inside contact with a fixed circle and are called in this connexion hypotrochoids. This curve becomes the ellipse when  $n$  is unity, and is familiar when  $n$  is three and  $a$  and  $b$  are equal as the astroid. The radius vector of the curve  $r$ , given by

$$r^2 = n^2 a^2 + b^2 + 2nab \cos (n+1)t,$$

is periodic in  $2\pi/(n+1)$ : the curve consequently consists of  $(n+1)$  similar arcs symmetrically oriented. When  $a$  and  $b$

are equal, the curve is star-shaped with  $(n+1)$  cusps; otherwise it has continuous curvature\*.

Fig. 1 shows specimens of the curves under discussion.

The fact that the curves treated in this paper possess points of inflexion, concave and convex arcs and cusps lends special interest to the solutions of the cylindrical conductors with these curves as cross-section. They give, in fact, interesting and comprehensive information as to the effect of curvature on the distribution of electricity on conductors, at the same time giving exact quantitative information in a wide and representative class of cases.

In a recent paper† H. W. Richmond has used the Schwarz-Christoffel transformation to obtain the solution of the two-dimensional electrostatic problems when the curve

Fig. 1.



of cross-section of the cylinder is made up of segments of any ellipses belonging to one confocal system and of their orthogonal trajectories, and his interesting adaptation of the transformation applied to any specific set of curves which form a set of equipotentials gives the solution when the cross-section of the cylinder is made up of segments of curves belonging to this set and to the set of their orthogonal trajectories. The set of equipotentials obtained in this paper can be used in the same way as the confocal ellipses, and a wide variety of curves of cross-section can be treated by taking curves made up of segments of any of the hypotrochoids belonging to one set of equipotentials and their orthogonal trajectories.

\* A discussion of the geometrical properties of these curves is given by Lamb, 'Infinitesimal Calculus,' pp. 297-307 (1919). The curves are easily described mechanically with a lathe; a number of interesting diagrams obtained in this manner are reproduced in R. A. Proctors 'Treatise on the Cycloid and Cycloidal Curves' (1878), which also contains an exhaustive account both of the history and of the geometrical properties of these curves.

† Proc. Lond. Math. Soc. (2) xxii. pp. 483-494 (1924).

I. *Freely Charged Cylinders.*

The equation of  $c$  the curve of cross-section of the cylinder is taken in the parametric form

$$\begin{aligned}x &= x(t) = na \cos t + b \cos nt \\y &= y(t) = na \sin t - b \sin nt\end{aligned}\quad (1)$$

with  $n$  a positive integer and  $b$  not greater than  $a$ . The radius vector from the centre of the curve is given by

$$r = r(t) = (n^2 a^2 + b^2 + 2nab \cos (n+1)t)^{\frac{1}{2}}.$$

The radius vector of the curve is therefore periodic in  $2\pi/(n+1)$  as a function of  $t$ : the curve, in fact, consists of  $(n+1)$  arcs symmetrically oriented about the centre, which is the centre of coordinates, and each of these arcs lies partly inside and partly outside the fundamental circle of radius  $na$ . The arc of the curve,  $s$ , is given by the equation

$$\begin{aligned}\dot{s}^2 &= (ds/dt)^2 = \dot{x}^2 + \dot{y}^2 \\&= n^2(a^2 + b^2 - 2ab \cos (n+1)t) \\&= n((n+1)(na^2 + b^2) - r^2).\end{aligned}$$

Further, the perpendicular from the centre on the tangent to the curve at any point  $t$  is given by

$$\begin{aligned}p^2 &= (x\dot{y} - y\dot{x})^2 / \dot{s}^2 \\&= \frac{(na^2 - b^2 - ab(n-1) \cos (n+1)t)^2}{[a^2 + b^2 - 2ab \cos (n+1)t]},\end{aligned}$$

or in terms of  $r$ , by the equation

$$p^2 = \frac{((n+1)(n^2 a^2 - b^2) - (n-1)r^2)^2}{4n[(n+1)(na^2 + b^2) - r^2]},$$

so that when  $a$  is equal to  $b$ , the  $(p, r)$  equation has the simple form

$$4np^2 = (n-1)^2((n+1)^2 a^2 - r^2),$$

and becomes, when  $n$  is unity,

$$p^2 = (a^2 - b^2)^2 / (2a^2 + 2b^2 - r^2),$$

the  $(p, r)$  equation for the ellipse with semi-axes  $(a+b)$  and  $(a-b)$ . The curvature  $c$  is given by

$$\begin{aligned}c &= 1/\rho = (x\dot{y} - y\dot{x})/\dot{s}^3 \\&= \frac{a^2 - nb^2 + (n-1)ab \cos (n+1)t}{n(a^2 + b^2 - 2ab \cos (n+1)t)^{\frac{3}{2}}}.\end{aligned}$$

When  $b$  is zero the curve becomes the circle and is everywhere concave to its centre. In the other extreme case,

when  $a$  and  $b$  are equal, the curve becomes the cusped hypocycloid and is everywhere convex to the origin. In the intermediate cases (the case  $n=1$  excepted), if the ratio  $b/a$  is sufficiently small, the curve is everywhere concave to the origin. For larger values of this ratio each arc of the curve is partly concave and partly convex, with the limiting case when  $b$  and  $a$  are equal as the only case in which the curve is wholly convex.

The equation of  $c$ , the curve (1), may be written in the form

$$z = x + iy = nae^{it} + be^{-nit}.$$

The complex variable

$$w = u + iv$$

is now introduced by the relation

$$z(w) = x(w) + iy(w) = nae^{iw} + be^{-niw}.$$

When  $v=0$   $z$  lies on the curve  $c$  with  $u$  equal to the parameter  $t$ . Also when  $v=-\infty$ ,  $z$  lies on the circle at infinity, with  $u$  equal to the argument of  $z$ . Finally

$$dz/dw = in(ae^{iw} - be^{-niw}),$$

and this is infinite only when  $v=-\infty$ , and zero only when

$$(n+1)v = \log(a/b) \geq 0, \quad \cos(n+1)t = 1.$$

When  $b$  and  $a$  are equal and the curve is cusped, those points at which  $dz/dw$  is zero lie on the curve at the cusps, otherwise they lie inside the curve. Consequently for points between the curves  $v=0$  and  $v=-\infty$ ,  $dz/dw$  is never infinite and never zero.

Using the variable  $w$ , we may now introduce the  $W$ -function

$$W = U + iV,$$

where  $V$  is the potential and  $U$  the corresponding conjugate function, given by

$$iW = iU - V = 2eiw + \text{constant}.$$

Then, on the curve  $c$ , which has been shown to be given by  $v=0$ ,  $V$  is constant. On the circle at infinity, which it will be convenient to call the curve  $C$ ,

$$V + 2e \log r = \text{constant}.$$

Further, between the curves  $c$  and  $C$ ,  $V$  has no singularities. These considerations are sufficient to show that  $V$  is the potential of the cylinder whose cross-section is the curve  $c$ , when it bears a charge  $e$  per unit length.





the  $v$ -levels of the function (2), being given by the equation

$$x = na e^{-v} \cos u + b e^{nv} \cos nu$$

$$y = na e^{-v} \sin u - b e^{nv} \sin nu$$

for values of  $v$  between zero and  $-\infty$ . Thus for example, the equipotentials associated with the curve

$$x = k(n \cos u + \cos nu)$$

$$y = k(n \sin u - \sin nu)$$

—which is the hypocycloid with  $(n+1)$  cusps—are the set of hypotrochoids

$$x = na \cos u + b \cos nu$$

$$y = na \sin u - b \sin nu,$$

in which

$$a^n b = k^{n+1}.$$

Any two hypotrochoids with parameters  $a_1$  and  $b_1$ ,  $a_2$  and  $b_2$  are therefore represented by two constant values of  $v$ , say  $v_1$  and  $v_2$ , in the transformation

$$z = k(n e^{i\pi} + e^{-ni\pi}),$$

provided that

$$a_1^n b_1 = a_2^n b_2,$$

the actual values of  $k$ ,  $v_1$ , and  $v_2$  being given by

$$k^{n+1} = a_r^n b_r, \quad v_r = \log(k/a_r). \quad (r=1, 2)$$

Thus we can at once find the capacity of a condenser consisting of two cylinders whose curves of cross-section are these two hypotrochoids. For if  $V_1$  and  $V_2$  are their potentials, we evidently have, for the potential in the region between them,

$$V = 2ev + \text{constant},$$

if the inner cylinder  $(a, b)$  has a charge  $e$  per unit length, and

$$V_1 - V_2 = 2e(v_1 - v_2) = 2e \log(a_2/a_1).$$

The capacity is consequently seen to be

$$1/(2 \log(a_2/a_1))$$

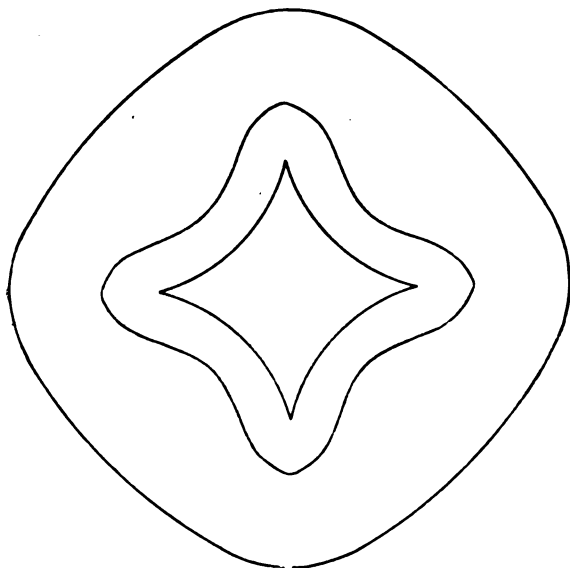
per unit length. It may be remarked that the capacity of the condenser in this case is identically equal to the capacity of two circular cylinders whose cross-sections are the fundamental circles of radius  $na_1$  and  $na_2$  associated with the hypotrochoids.

And it is worthy of notice that the set of hypotrochoids  $(a, b)$  of any specific positive integral order  $n$  form an equipotential set, so long as  $a^n b$  has a constant value, the

innermost member of such an equipotential set being the hypocycloid with  $(n+1)$  cusps. These results will be seen to provide a wide generalization of the equipotential character of sets of confocal ellipses, which on this occasion present themselves in the unwonted aspect of hypotrochoids, the innermost member of the family, the straight line ellipse, being only with difficulty recognized under the elaborate designation of the "two-cusped hypocycloid."

Fig. 2 gives a sketch of the hypotrochoids of order three which form a set of equipotentials.

Fig. 2.



### III. *Cylinders in a Uniform Field.*

Suppose the cylinder  $c$  with cross-section

$$x = na \cos t + b \cos nt$$

$$y = na \sin t - b \sin nt$$

is placed in a uniform field of electric force given by

$$iW_0 = f_0 + fz e^{-i\alpha},$$

so that

$$-V_0 = f_0 + f(x \cos \alpha + y \sin \alpha),$$

$$U_0 = f(y \cos \alpha - x \sin \alpha).$$

Let

$$iW_1 = iU_1 - V_1$$

represent the disturbance due to the presence of the cylinder, and let

$$iW = iU - V$$

be the  $W$ -function for the field when the cylinder is present, so that

$$iW = iW_0 + iW_1.$$

The conditions of the problem will be satisfied if  $V_1$  is a solution of Laplace's equation evanescent on the circle at infinity and such that  $V_0 + V_1$  is constant on the curve  $c$ , having no singularities in the region between the circle at infinity and the curve  $c$ .

We again use the complex variable  $w$  defined by the relation

$$z = nae^{i\epsilon} + be^{-ni\epsilon},$$

so that  $v=0$  is the curve  $c$  with  $u=t$  and  $v=-\infty$  is the circle at infinity. Then in terms of  $w$ ,

$$iW_0 = f_0 + f(nae^{i\epsilon-i\alpha} + be^{-ni\epsilon-i\alpha}),$$

so that

$$-V_0 = f_0 + f(nae^{-v} \cos(u-\alpha) + be^{nv} \cos(nu+\alpha)).$$

Then put

$$-V_1 = -f(nae^v \cos(u-\alpha) + be^{nv} \cos(nu+\alpha)),$$

and consequently

$$iW_1 = -f(nae^{-i\epsilon+i\alpha} + be^{-ni\epsilon-i\alpha}),$$

for then

$$\begin{aligned} iW &= f_0 + 2niaf' \sin(w-\alpha), \\ -V &= f - 2naf' \cos(u-\alpha) \sinh v, \\ U &= 2naf' \sin(u-\alpha) \cosh v, \end{aligned}$$

which makes  $V$ , on the curve  $c$ , equal to  $-f$ , the potential at the centre of the curve in the undisturbed field: and  $V_1$  is evanescent on  $v=-\infty$  and without singularities between  $c$  and the circle at infinity.

The surface density  $\sigma$  at any point  $t$  is given by

$$4\pi\sigma = 2fa \cos(t-\alpha)/(a^2+b^2-2ab \cos(n+1)t)^{\frac{1}{2}}.$$

The total amount of electricity separated on the cylinder per unit length is evidently  $nfa/\pi$ , the amount separated per unit length on a circular cylinder of radius  $na$ .

## 702 *Some Problems of Two-Dimensional Electrostatics.*

The solution for the hypocycloidal cylinders—for which  $a$  and  $b$  are equal—is of special interest. We have

$$4\pi\sigma = f \cos(t - \alpha) / \sin \frac{1}{2}(n+1)t.$$

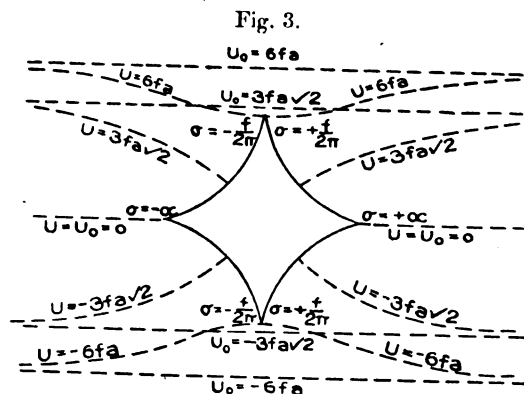
In general, therefore, there will be infinities for  $\sigma$  at the  $(n+1)$  cusps, the sign of these infinities being determined by the sign of  $\cos(t - \alpha)$ . If, however, the field is perpendicular to the tangent at a cusp  $t_0$ , so that  $\cos(t_0 - \alpha)$  vanishes, the infinity for  $\sigma$  at this cusp will disappear and instead there will be a jump in the value of  $\sigma$  from the value

$$\sigma = -\frac{1}{2}f/(n+1)\pi$$

at the point  $t = t_0 - 0$ , to the value

$$\sigma = +\frac{1}{2}f/(n+1)\pi$$

at the point  $t = t_0 + 0$ . Thus there will either be infinities at all the  $(n+1)$  cusps: or when  $n$  is odd, infinities at  $n$  cusps



and a discontinuity at a single cusp, and when  $n$  is even, infinities at  $(n-2)$  cusps and discontinuities at two diametrically opposite cusps. Fig. 3 shows the distribution of electricity and the lie of the lines of force in the case of the astroid ( $n=3$ ) when the field is along an axis of the curve and there are consequently infinities at the two cusps on this axis and discontinuities at the other two cusps.

### IV. *Application of the Schwarz-Christoffel Transformation.*

By means of an adaptation of the Schwarz-Christoffel transformation, the solution is obtained of the electrostatic

problems relating to a cylinder whose curve of cross-section is made up of segments of the hypotrochoids

$$x = na \cos t + b \cos nt,$$

$$y = na \sin t - b \sin nt,$$

with  $a^n b$  equal to some constant, say  $k^{n+1}$ , and their orthogonal trajectories. For with the transformation

$$z = k(ne^{i\pi} + e^{-i\pi})$$

such a curve of cross-section is represented in the  $w$ -plane by segments of lines parallel to the axes of  $u$  and  $v$ ; to such a curve the Schwarz-Christoffel method can at once be applied. The solutions of two-dimensional electrostatic problems are therefore available in a very wide set of subsidiary cases and can easily be worked out by means of a double transformation, if they are required. It is unnecessary to point out the fact that these solutions—in marked contradistinction to the solutions for cylinders of hypotrochoidal cross-section given in this paper—are by no means suitable for practical application, since they involve, in general, integrals of complicated elliptic and hyperelliptic type\*.

LXX. *The Critical Pressure-Ratio for Gases as affected by Variable Specific Heat.* By W. J. WALKER, Ph.D., University College, Dundee †.

# *Summary.*

IN a previous paper in the 'Philosophical Magazine' for March 1922, the analysis involving the effect of variable specific heat on the discharge of gases through orifices or nozzles was given, and certain important conclusions were drawn therefrom. In the present note the critical pressure-ratio determining the maximum discharge condition under variable specific heat conditions has been deduced. The

\* Reference should be made to the paper by H. W. Richmond already cited. Results are there obtained by reference to confocal ellipses and their orthogonal trajectories, the confocal hyperbolae, in virtue of the equipotential character of these families of curves. By reference to the sets of hypotrochoids, whose equipotential character is demonstrated in this paper, and their orthogonal trajectories, powerful generalizations of these results may be obtained.

† Communicated by the Author.

result obtained shows that this critical pressure-ratio is higher the higher the temperatures involved, and is also higher than under constant specific heat conditions.

Under adiabatic conditions of flow from a region of higher pressure  $p_1$  to one of lower pressure  $p_2$ , the velocity of flow of a gas is given by

$$u_2^2 - u_1^2 = 2g(I_1 - I_2), \quad . . . . . (1)$$

$u$  denoting velocity in feet per second, and  $I$  denoting total heat energy in ft.-lb. per lb. The total heat-energy change involved in giving the gas this kinetic energy during expansion is

$$= \int_{T_2}^{T_1} dI = \int_{T_2}^{T_1} v dp,$$

$v$  denoting specific volume in cubic ft. per lb., and  $p$  denoting pressure in lb. per sq. ft.

To a first and close approximation this may be written

$$I_1 - I_2 = \left( \frac{p_1 v_1 - p_2 v_2}{m-1} \right) \left\{ 1 + \frac{\lambda}{2R} (p_1 v_1 + p_2 v_2) \right\} + p_1 v_1 - p_2 v_2,$$

$\lambda$  being small in relation to other factors and having the same signification as in previous papers.

$$\begin{aligned} \therefore I_1 - I_2 &= \frac{m}{m-1} \{ p_1 v_1 - p_2 v_2 \} \left\{ 1 + \frac{\lambda}{2mR} (p_1 v_1 + p_2 v_2) \right\} \\ &= \frac{mR}{m-1} \{ T_1 - T_2 \} \left\{ 1 + \frac{\lambda}{2m} (T_1 + T_2) \right\}. \quad . . . (2) \end{aligned}$$

Now, the velocity of sound in a gas under specific volume  $v$  and pressure  $p$  is given by

$$\begin{aligned} C &= \sqrt{\frac{\bar{K}}{\bar{K}_v} gpv}, \\ &= \sqrt{mgrp} \left\{ 1 - \lambda T \left( \frac{m-1}{m} \right) \right\} \text{ to a first and close approximation,} \\ &= \sqrt{mgRT} \left\{ 1 - \lambda T \left( \frac{m-1}{m} \right) \right\}. \quad . . . . . (3) \end{aligned}$$

Assuming, as is usually very nearly true under most practical conditions, that  $u_1$  is negligible in relation to  $u_2$ , then equations (1), (2), and (3) combined give

$$u_2^2 = \frac{2}{m-1} \{ C_1^2 - C_2^2 \} \left\{ 1 + \frac{\lambda(2m-1)}{2m} (T_1 + T_2) \right\}. \quad . . . (4)$$

Now, the critical pressure-ratio must, just as under constant specific heat conditions, be that producing a gas-discharge velocity equal to the velocity of sound through the gas under the conditions prevailing at the discharge side. From (4), therefore, since  $u_2 = C_2$  at the critical pressure-ratio,

$$\begin{aligned} u_2^2 \left\{ 1 + \frac{m-1}{2} + \frac{\lambda(2m-1)}{2m} (T_1 + T_2) \right\} \\ = C_1^2 \left\{ 1 + \frac{\lambda(2m-1)(T_1 + T_2)}{2m} \right\}; \\ \therefore T_2 \left\{ 1 - \lambda T_2 \left( \frac{m-1}{m} \right) \right\} \left\{ 1 + \frac{m-1}{2} + \frac{\lambda(2m-1)}{2m} (T_1 + T_2) \right\} \\ = T_1 \left\{ 1 - \lambda T_1 \left( \frac{m-1}{m} \right) \right\} \left\{ 1 + \frac{\lambda(2m-1)(T_1 + T_2)}{2m} \right\}; \\ \therefore \frac{m+1}{2} T_2 \left[ 1 - \lambda T_2 \left\{ \frac{(m-1)}{m} - \frac{(2m-1)(m+3)}{2m(m+1)} \right\} \right] \\ = T_1 \left[ 1 - \lambda T_2 \left\{ \frac{(m-1)(m+1)}{2m} - \frac{(2m-1)(m+3)}{4m} \right\} \right]; \\ \therefore \frac{m+1}{2} T_2 = T_1 \left\{ 1 + \lambda T_2 \frac{(5m-1)(m-1)}{4m(m+1)} \right\}. \quad (5) \end{aligned}$$

But, under adiabatic conditions of flow,

$$\begin{aligned} \frac{p_2}{p_1} &= \left( \frac{T_2}{T_1} \right)^{\frac{m}{m-1}} e^{\frac{\lambda(T_2 - T_1)}{m-1}}, \\ &= \left( \frac{T_2}{T_1} \right)^{\frac{m}{m-1}} \left\{ 1 + \frac{\lambda(T_2 - T_1)}{m-1} \right\} \quad \text{to a first and close approximation,} \\ &= \left( \frac{T_2}{T_1} \right)^{\frac{m}{m-1}} \left\{ 1 - \frac{\lambda T_2}{2} \right\}. \end{aligned}$$

Therefore from (5)

$$\frac{p_2}{p_1} = \left( \frac{2}{m+1} \right)^{\frac{m}{m-1}} \left\{ 1 + \frac{3\lambda T_2(m-1)}{4(m+1)} \right\}. \quad (6)$$

Under constant specific heat conditions the critical ratio is usually given as

$$\frac{p_2}{p_1} = \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma}{\gamma-1}},$$

where  $\gamma = \frac{K_p}{K_v}.$



The term in double brackets in (6) therefore represents the effect due to variable specific heat.

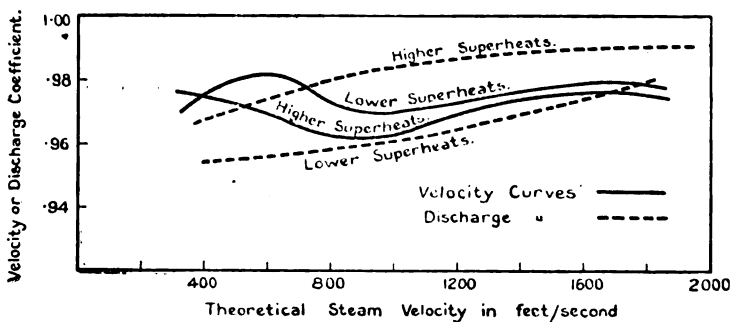
The inferences to be drawn from (6) are that the critical pressure-ratio

- (1) Varies as the temperature is altered, and
- (2) Diminishes or increases according to whether the specific heat of the gas diminishes or increases respectively with rise of temperature.

It should be noted that at normal temperatures the value of the term

$$\frac{3\lambda T_2(m-1)}{4(m+1)}$$

is practically negligible. Thus for an average internal combustion engine working fluid,  $\lambda = 0.00283$  approx. when  $T$  is in  $^{\circ}\text{C}$ . absolute. Taking  $T_2 = 288^{\circ}\text{C}$ . absolute, the value of the term becomes 0.0102 when  $m$  is assumed equal to 1.4. At the higher temperatures, however, it may have quite appreciable values.



It may reasonably be claimed that the formulæ thus derived, as given by the writer in this and previous papers, give very close approximation to the actual effect of variable specific heat. This is borne out by the following further recent remarkable verification of the formulæ given in the previous paper in the 'Philosophical Magazine,' March 1922.

In the Third Report of the Steam Nozzles Research Committee, published in the 'Proceedings of the Institution of Mechanical Engineers,' May 1924, the velocity and discharge coefficient curves, reproduced here in the diagram, are published. The experiments from which these curves have been derived have been carried out under conditions conducive to the highest accuracy, and there is no reason to doubt their validity.

Both the velocity and discharge coefficients for these curves

have been calculated from the tests by the application of Callendar's equations, and, as will be observed from the figure, the velocity and discharge curves occupy reversed positions in relation to superheat. Since  $\lambda$ , for superheated steam, is negative within the experimental range concerned, this is exactly what should occur according to the writer's variable specific heat equations for velocity and discharge if variable specific heat is neglected or not sufficiently taken into account. Not only so, but in further conformity with these equations, which show that the percentage error due to neglect of variable specific heat in calculating the discharges will be three times the error made in calculating the velocities, it will be observed from the reproduced curves that even this secondary result is verified, the difference between the dotted or discharge coefficient curves being decidedly more marked than that between the full line or velocity coefficient curves. This agreement can scarcely be accidental, and it does not appear possible that any valid argument based on friction effects or variation in coefficient of contraction can be adduced to nullify it.

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LXXI. *On the Irregularity of the  $L\alpha$  Doublet in the X-ray Spectra.* By B. B. RAY, D.Sc. (Lecturer, Calcutta University)\*.

### 1. Introduction.

THE normal electronic arrangement about the nucleus, according to Bohr, should be such as would result from the capturing of electrons, one at a time, by the structure, each electron occupying that orbit which is most stable with respect to the nucleus and previously bound electrons. Following this scheme, one would find 2 electrons in the K-shell, 8 in the L-shell, 18 in the M-shell, and so on, in the elements of higher atomic numbers. The influence of a newly added electron in higher elements is very small, amounting practically to nothing in the innermost shells. If this view be accepted, then as one goes from lower to higher elements the influence of electrons in the outer shells should gradually decrease to zero in the K or L-shells. If the  $K\alpha$  doublet, i. e. the difference in wave-length between  $K\alpha_1$  and  $K\alpha_2$ , which is formed by the jumps of electrons from the L-shell to the K-shell, is examined from the lower to the higher elements, one would find that the gradual increase in  $\Delta\lambda$  of the  $K\alpha$  doublet is more rapid in the lower elements than the higher ones, and in the latter this value ( $\Delta\lambda$ ) ultimately tends to be almost constant. But

\* Communicated by Prof. Manne Siegbahn.

the newly added electron is not always added to the outermost shell, and there are regions where it goes rather to the inside shell, thus increasing the number in this shell, and forming a more stable arrangement; this we find in the elements from Ti (22) to Cu (29). In the former we have 4, 4, 2 electrons in the M-shell and 2 electrons in the N-shell, but in the latter we have 6, 6, 6 electrons in the M-shell and 1 in the N-shell. Thus in this arrangement, as the electrons in the L-shell are influenced by those of the next outer shell M, some changes are to be expected in the  $K\alpha$  doublet in this region. So also in the elements from Al (13) to A (18). In a former paper, Siegbahn and the author\* studied the  $K\alpha$  doublet in these regions, and changes as expected from the Bohr scheme were actually found. It thus appeared that in the higher elements, where such changes should occur in the N-shell as expected by Bohr, the  $L\alpha$  doublet would be affected, and by studying the doublet, such changes may be observed. According to Bohr the electrons are arranged in the following way and we quote them only from Y (39) to Th (90) as relevant to this paper.

$\searrow$ $nK$ . Z.	K. 1 <sub>1</sub>	L. 2 <sub>1</sub> 2 <sub>2</sub>	M. 3 <sub>1</sub> 3 <sub>2</sub> 3 <sub>3</sub>	N. 4 <sub>1</sub> 4 <sub>2</sub> 4 <sub>3</sub> 4 <sub>4</sub>	O. 5 <sub>1</sub> 5 <sub>2</sub> 5 <sub>3</sub> 5 <sub>4</sub> 5 <sub>5</sub>	P. 6 <sub>1</sub> 6 <sub>2</sub> 6 <sub>3</sub> 6 <sub>4</sub> 6 <sub>5</sub> 6 <sub>6</sub>	 7 <sub>1</sub> 7 <sub>2</sub>
39 Y	2	4 4	6 6 6	4 4 1	(2)		
40 Zr	2	4 4	6 6 6	4 4 2	(2)		
47 Ag	2	4 4	6 6 6	6 6 6	1		
48 Cd	2	4 4	6 6 6	6 6 6	2		
49 In	2	4 4	6 6 6	6 6 6	2 1		
54 X	2	4 4	6 6 6	6 6 6	4 4		
55 Cs	2	4 4	6 6 6	6 6 6	4 4	1	
56 Ba	2	4 4	6 6 6	6 6 6	4 4	2	
57 La	2	4 4	6 6 6	6 6 6	4 4 1	(2)	
58 Ce	2	4 4	6 6 6	6 6 6 1	4 4 1	(2)	
59 Pr	2	4 4	6 6 6	6 6 6 2	4 4 1	(2)	
71 Lu	2	4 4	6 6 6	8 8 8 8	4 4 1	(2)	
72 Hf	2	4 4	6 6 6	8 8 8 8	4 4 2	(2)	
79 Au	2	4 4	6 6 6	8 8 8 8	6 6 6	1	
80 Hg	2	4 4	6 6 6	8 8 8 8	6 6 6	2	
81 Tl	2	4 4	6 6 6	8 8 8 8	6 6 6	2 1	
86 Nt	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	
87 —	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	1
88 Ra	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	2
89 Ac	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 1	(2)
90 Th	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 2	(2)

\* Arkiv för Matematik, Astronomie och Fysik, Band 18, No. 19.

From the above scheme the changes are to be expected from the elements Zr (40) to Ag (47) and Pr (59) to Lu (71).

## 2. Experimental Observations.

A Hadding tube was connected to an aluminium spectrograph, the width of the slit being 0.09 mm., and the photographic plate was placed at a distance of 12.15 cm. from the axis of the rotating face of the crystal. A current of 10 milliamp. at about 50 kilovolts was passed through the tube. The spectrograph was connected to an oil pump when vacuum was necessary within it. In the  $L\alpha$  doublet,  $\alpha_1$  is a strong line and  $\alpha_2$  is rather weak, so that to get a good impression of  $\alpha_2$ , a rather long time (about 1 hour) is necessary, and this makes the strong line  $\alpha_1$  broad, thus increasing the error in the measurements of the distance between the lines. Several measurements are taken and the mean value of  $\Delta\lambda$  is tabulated below. The values for Nb and Mo were kindly supplied by Mr. A. Larsson, and the value for U was taken from Siegbahn's table. Some plates were also taken in the higher order to check the result.

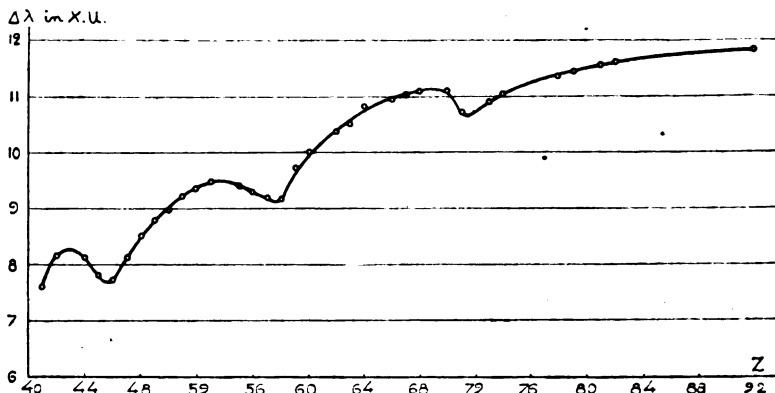
TABLE I.

Z.	$\Delta\lambda$ in X.U.	Z.	$\Delta\lambda$ in X.U.
41 Nb .....	7.58	60 Nd .....	10.05
42 Mo .....	8.23	62 Sm .....	10.35
44 Ru .....	8.15	63 Eu .....	10.50
45 Rh .....	7.78	64 Gd .....	10.81
46 Pd .....	7.72	66 Dy .....	10.95
47 Ag .....	8.16	67 Ho .....	11.02
48 Cd .....	8.51	68 Er .....	11.10
49 In .....	8.80	70 Yb .....	11.12
50 Sn .....	8.95	71 Lu .....	10.69
51 Sb .....	9.22	73 Ta .....	10.93
52 Te .....	9.40	74 W .....	11.02
53 I .....	9.48	78 Pt .....	11.39
55 Cs .....	9.42	79 Au .....	11.45
56 Ba .....	9.33	81 Tl .....	11.53
57 La .....	9.22	82 Pb .....	11.54
58 Ce .....	9.18	92 U .....	11.81
59 Pr .....	9.74		

A curve is also drawn with  $d\Delta$  as ordinate and Z as abscissa.

## 710 *Irregularity of the $L\alpha$ Doublet in X-ray Spectra.*

From the figure it will be observed that the changes as expected from the Bohr model come out in a general way. As the  $\alpha_1$  line is rather broad it is necessary to examine whether the bends in the curve, especially in the regions Pd (46), Ce (58), and Lu (71), are due to experimental errors. In order to test this point, the highest values of  $\Delta\lambda$  as measured from the plate in these elements were taken together with the smallest values of  $\Delta\lambda$  in the elements Rh (45), Ag (47), Cs (55), Ba (56), Pr (59), Yb (70),



Ta (73); and W (74); it is found that the bends can still be seen as in fig. 1, thus proving the reality of the changes of the  $L\alpha$  doublet in these elements.

### 3. *Changes of $\alpha_1$ and $\alpha_2$ .*

Some calculations are made in the  $L\alpha$  doublet like those in the  $K\alpha$  doublet, to determine whether the changes as observed in the figure may be due to the change of any one of them. But it is found that both the  $\alpha_1$  and  $\alpha_2$  lines undergo similar changes. In the ordinary relativity theory,  $\alpha_1$  (L series) results from the jump of an electron from the  $3_3$  orbit to the  $2_2$  orbit, whereas  $\alpha_2$  results from a jump from  $3_2$  to  $2_2$ . It is natural then to suppose on this view that  $\alpha_2$  should change more than  $\alpha_1$ , as the orbit  $3_3$  is circular and the orbit  $3_2$  is elliptical, and the influence of a newly added electron will be more felt by an elliptical orbit than by the circular one. But no such conclusion can be arrived at from our calculation. This result may be truly anticipated from the new suggestion about the formation of X-ray lines, just put forward by Landé\*, whereby he assumes that

\* *Zeit. f. Fys.* May 1924.

electrons in both the  $M_1$  and  $M_2$ -shell move in orbits of the same shape but different orientations.

My thanks are due to Prof. M. Siegbahn for suggesting the problem and taking keen interest during the progress of the work. My thanks are also due to Mr. R. Thoraens and Mr. A. Larsson.

Physical Laboratory,  
Upsala University, Sweden.

LXXII. *The Mobility in Air of Ions produced in another Gas.*  
By G. C. GRINDLEY, B.Sc., and Professor A. M. TYNDALL, D.Sc.\*

WHILE many determinations of the mobility of gaseous ions have been made with a view to elucidating their nature, there is by no means unanimous agreement on the conclusions to be drawn from the results. Among some of the more interesting experiments may be classed those which deal with the mobility of ions formed in one gas and measured in another. Let us take for example the equation for mobility deduced from dynamical considerations by Langevin in 1905†:

$$K = \frac{.505}{\sqrt{P(K-1)}} \sqrt{1 + \frac{m}{M}},$$

where  $m$  = mass of molecule and  $M$  = mass of ion.

Let us then calculate the ratio of the mobility of a charged foreign ion in oxygen to that of an oxygen ion in oxygen on the (arbitrary) assumption that an ion is a charged molecule of the gas in which it was originally formed. The following figures are obtained:—Hydrogen 2.82, ammonia 1.20, carbon dioxide 0.93, ether 0.85, chloroform 0.80, recoil atoms from ThD 0.76. Heavier ions give a ratio approaching the limit 0.71 when their mass is infinite. The figures are not materially altered by substituting air for oxygen.

Four independent investigations have been made by Rutherford‡, Franck§, Blanc||, and Wellisch¶, and the

\* Communicated by the Authors.

† Langevin, *Ann. de Chim. et de Phys.* (8) v. p. 245 (1905).

‡ Rutherford, *Phil. Mag.* v. p. 95 (1903).

§ Franck, *Deut. Phys. Gesell.* v. p. 397 (1909).

|| Blanc, *Journ. de Phys.* vii. p. 825 (1908).

¶ Wellisch, *Proc. Roy. Soc.* lxxii. p. 500 (1909).

conclusion has been reached that the ion acquires a mobility which is independent of the gas in which it was formed, and cannot be distinguished from an ion formed directly in the gas in which the measurements are made. Rutherford's experiment was carried out with the positively-charged recoil atoms from radium and thorium emanation. The conclusion was that their mobility lay between 1.0 for radium and between 1.17 and 1.7 for thorium emanation—that is to say, was of the same order of magnitude as air ions.

Franck used the recoil atoms from ThD. He found that the mobility of these carriers in air was 1.56 and in hydrogen 6.21. In both cases the values are higher than the mean values of other experimenters for ordinary positive ions in these gases, the difference in air being as much as 10 per cent. The fact that the value is greater and not smaller, as might have been expected for such heavy atoms, suggests that the accuracy of a method depending on the deposition of active material on a plate is not great. A second experiment by Franck and Meitner\* by another method gave limits to the mobility of these carriers in air, namely  $>0.7$  and  $<1.6$ †.

The experiments of Blanc were made by filling a dish with  $\text{CO}_2$ , ionizing it with radium, and drawing ions of the appropriate sign into the air-space above and measuring their mobility by the Rutherford alternating field method. The experiment was then repeated without  $\text{CO}_2$ , and it was found that the curves obtained in the two cases were in good agreement. But the experiment takes time, and the objection may therefore be raised that owing to convection and diffusion the  $\text{CO}_2$  may have disappeared from the dish, and that consequently mainly air ions were being experimented upon in both cases.

The experiments of Wellisch are much more conclusive. Apart from showing that a mixture of gases such as oxygen and sulphur dioxide, or of ethyl ether and air, gave ions of a single value of mobility and not two values (in itself a very significant result), Wellisch carried out the following experiment. He took methyl iodide, which is strongly ionized by X-rays at 6 mm. pressure, filled up the vessel

\* Franck & Meitner, *Deut. Phys. Gesell.* xiii. p. 671 (1911).

† As this paper is being sent for publication, an abstract of a paper read by Erikson before the American Physical Society has appeared in the 'Physical Review' (June 1924). He claims to have discovered two groups of ions of Actinium B in air, of mobility 3.15 and 1.20 respectively. He used air-velocities of 2000 cm./sec.; and until full details appear, one cannot help feeling that results obtained with such high air-speeds (involving eddies) must be viewed with caution.

with hydrogen to atmospheric pressure, and made a measurement of mobility by a modification of Langevin's method. He argued, with reason, that this was virtually a determination of the mobility in hydrogen of ions produced by the action of X-rays on methyl iodide. His conclusions were the same as those of Blanc.

To sum up, the experiments of Wellisch, and probably also those of Franck, make it clear that differences of the order of magnitude which the above calculation gives for the ions they used did not exist. Wellisch in consequence adopted the idea of an ion as a single molecule with a transferable charge, though Franck pointed out the difficulty of this hypothesis in the case of positive recoil atoms.

An apparatus used by the writers\* for another purpose being readily available and apparently likely to give comparative results of a high order of accuracy, it was felt that further tests of this type were worth making, particularly with a view to their extension to hydrogen, ammonia, or any other substance lighter than air. If, for instance, one adopts the alternative view that an ion is a cluster of molecules loosely held to an ionized molecule and shed and replaced by other molecules when it passes into another gas, then if a small difference in mobility could be observed in any particular case, it might throw some light on the problem of the size of a cluster. If, for instance, on Langevin's formula we compare the mobility in air of a charged hydrogen molecule with that of a chloroform molecule when each of them is loaded with, say, 6 molecules of air, we should expect a ratio of 1.03, which should be readily detectable.

Briefly, the principle of this method was to produce the ions by polonium in a vessel A (fig. 1), to draw ions of one sign by an electric field through a slit  $S_1$  into a long, shallow box through which filtered dry air was flowing, to drag them across the air-stream by another field, and to catch them on the other side of the box at another slit  $S_2$ , which was adjustable in position relative to  $S_1$ . Under given conditions the displacement of the ions downstream is a measure of their mobility. Owing, however, to diffusion the ions do not all travel along the same path, but reference to the original paper will show that the distribution curve at  $S_2$  gives a well-defined peak from which measurements may be made. The method was slightly modified in the present work. Instead of keeping

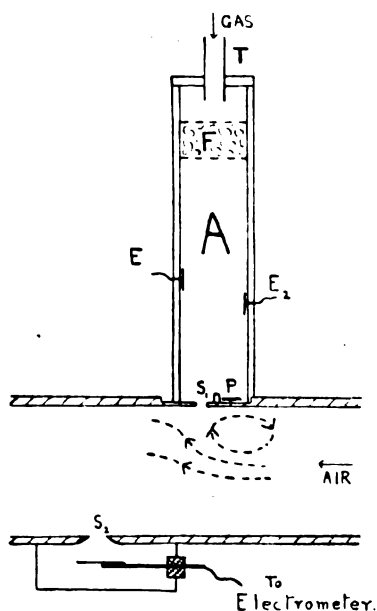
\* Tyndall & Grindley, *Phil. Mag.* April 1924.



the potential difference between the two sides of the box constant, and moving one slit relative to the other, the slits were kept fixed and the potential difference varied. It was found that this method gave somewhat sharper peaks than the earlier one.

The true position of the peak was estimated by taking several pairs of points symmetrically situated on a smooth curve through the observations, finding the mean voltage in each case, and averaging the results. The value obtained was in no case very different from that of the apparent peak of the smoothed graph.

Fig. 1.



Now, if the box A is filled with a particular gas, the ions will be formed in this gas, while their mobility measurement will be made in another—namely air. If previous experimenters are right in their conclusion that the measured mobility will be that of air ions and independent of the nature of the gas in which the ions were formed, then the position of the peak in the distribution curve at  $S_2$

will be the same whether the vessel A is filled with air or with a foreign gas.

The vessel A was an airtight ebonite box (8 in.  $\times$  2 in.  $\times$  1 in.), into which the gas was introduced by means of a tube T. Some polonium, P, which ionized the gas above S, was so arranged that none of its  $\alpha$  particles could pass through the slit. A layer of cottonwool F acted as a dust-filter; and ensured an approximately even flow of gas in the lower part of A. Two electrodes  $E_1$  and  $E_2$  (connected together) were arranged so that by applying a suitable potential to them a concentrated stream of ions could be directed to  $S_1$ .

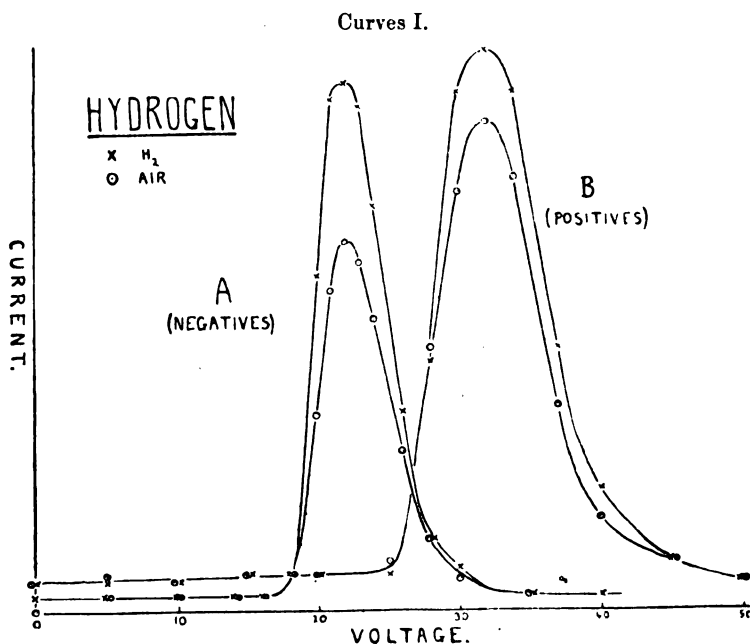
The method first adopted was to fill A by a rapid stream of gas through T, and then to cut A off from the supply while a reading of the electrometer was being taken. The peaks obtained in this way, however, were not identical in position with those due to normal air ions; but by mixing smoke with the air-stream through the box, the cause of this was shown to be eddy currents at the slit  $S_1$  due to the difference in density between the two gases. Fig. 1, for instance, gives a rough indication of the eddy currents observed by smoke when the box A was placed above  $S_1$  and was filled with hydrogen. It is clear from this that in the neighbourhood of  $S_1$  there was an upward current tending to retard the motion of the ions across the box to  $S_2$ . Owing to this the apparent mobility would be too low; and this was exactly what the voltage curves indicated, the potential difference required to give the maximum current at  $S_2$  being greater in the case of hydrogen than in the case of air. The effect was also found with coal-gas, and to a very slight extent with ammonia. The absence, however, of any second peak in the curves showed that the ions were homogenous.

In order to obtain a true mobility test, therefore, it was necessary to cut down the effect of these eddies as far as possible; and this was done by using a high velocity of air-current, by making the slit  $S_1$  as narrow as possible (the width was cut down from 4 mm. to 2 mm.), and by taking the electrometer readings, when necessary, while a slow steady stream of the gas was being passed through T and  $S_1$ . Tests with smoke showed that under these conditions the disturbing upper eddy currents at the slit were (as far as one could see) eliminated.

The results obtained may be divided into two classes, according as the gas in A was (1) lighter, (2) heavier than air.

## LIGHT GASES.

*Hydrogen.*—The hydrogen was prepared in a kipp from sulphuric acid and zinc, and passed through potassium permanganate and lead acetate solutions, pure sulphuric acid, and calcium chloride. The type of curve obtained is shown in Curves I. A and B, where the current received by the electrometer is plotted with voltage across the box. The crosses give the curves for ions produced in A filled with hydrogen, the circles for ions produced in A filled with air. Within the limits of experimental error the peaks for positive and



negative ions occur in each case at the same voltage, whichever gas supplied the ions originally. Taking a number of such graphs, the mean ratio of voltages—i. e. the ratio of mobilities—for hydrogen and air was 0.993 for positive and 1.006 for negative. This result is, however, not conclusive without further tests. It might be argued that owing to diffusion through  $S_1$  the hydrogen was not pure, and that the density of ionization of the heavier air impurity in A was much greater than that of the hydrogen, thus giving a supply of ions which was mainly of air from the start. The results of drawing off samples of gas from A and

analysing them were not very conclusive, because air tended to be sucked into A through the slit  $S_1$  in the process. The method referred to above of allowing a continuous slow stream of hydrogen to pass through A and out at  $S_1$  served the double purpose of cutting down the eddy effect and improving the purity.

It is difficult to believe that under these circumstances the gas in A contained more than a small percentage of air. It might be argued even then that, despite their greater diffusion, hydrogen ions, owing to their higher mobility, will be trapped by the edges of the slit more readily than air ions, and that consequently relatively few of them will find their way into the air channel; but a subsidiary experiment with pure hydrogen above and below a slit showed that this was not the case. This being so, even if in the original experiment some air was present in A, there must have been an appreciable amount of hydrogen ions formed there which, had they retained their identity in the air-stream, would have given rise to a second peak somewhere in the curve. A careful test of the current supplied to  $S_3$  was made over a wide range of voltage, without any suggestion of a second peak being found.

Finally, there was the possibility that the distortion of the field at  $S_2$  due to the sharp edges gave rise to a similar sorting of ions of different mobilities, thus preventing hydrogen ions from reaching the electrometer. To show that this was not the case, a wire connected to the electrometer was inserted in  $S_2$  flush with the surface, and on some occasions a potential of a volt or two was applied between it and the edges of the slit. Again, only one peak was observed, and this coincided with that appropriate to air ions.

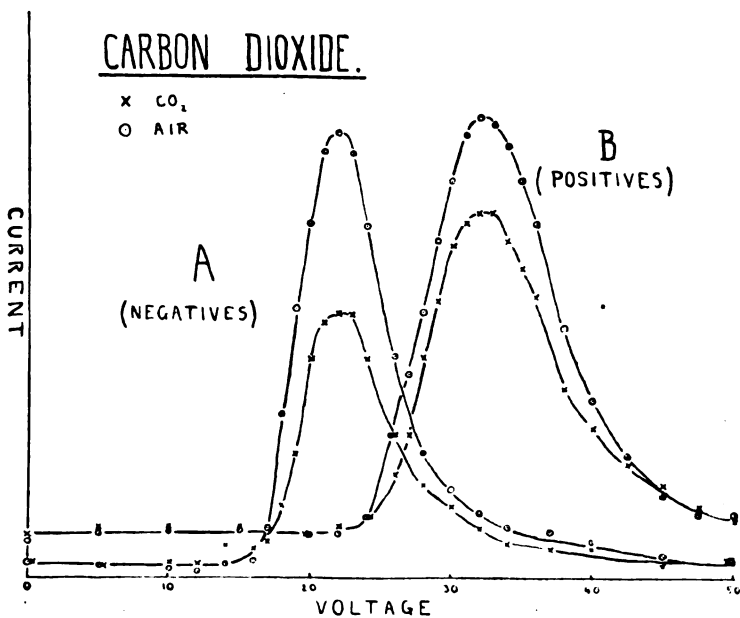
*Ammonia.*—The supply of ammonia was obtained by driving the air slowly through cotton-wool saturated in ammonia solution, and by placing in A cotton-wool soaked in ammonia solution. The graphs obtained were similar to those with hydrogen, the identity of the voltages at the peaks being shown by the following ratio for ammonia ion and air ion: positive ions = 0.991, negative ions = 1.003.

#### HEAVY GASES.

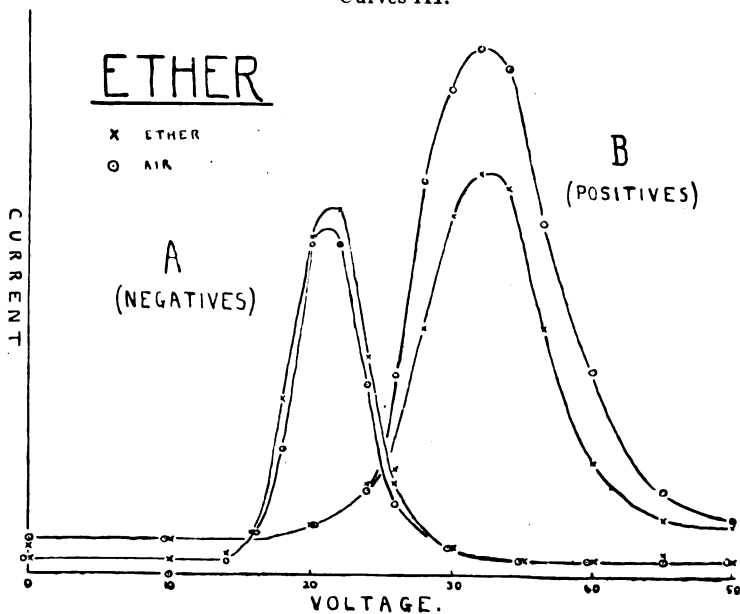
For this purpose the arrangement shown in fig. 1 was inverted, the chamber A being placed under the main mobility box.

*Carbon dioxide.*—The gas was prepared from marble and

Curves II.



Curves III.



hydrochloric acid and dried. The results are graphed in Curves II.; from such graphs the mean ratios for the voltages were: positive 1·001, negative 0·991.

*Ether.*—The air in A was saturated with ether by placing round its inner surface a layer of flannel soaked in ether. Curves III. show the graphs obtained, for which the ratios are: positive 1·004, negative 0·995.

*Chloroform.*—In this case liquid chloroform was placed in A. The ratios obtained were: positive 1·000, negative 1·006.

Incidentally, it may be pointed out that if all the results are grouped together, the value obtained for the ratio of the mobilities of negative and positive ions is very close to 1·50. This agrees more closely with the recent values of Loeb and of Wellisch than with earlier results.

### *Conclusions.*

In all cases there is agreement in the position of the voltages at the peaks for air and the gas in question to under 1 per cent. That is to say, there is no sensible difference between the mobility of ions produced directly in air and that of ions produced in another gas or vapour and measured in air. This result agrees with the previous conclusion of Wellisch and others. But the agreement is probably more accurate, and moreover extends to other ionized gases and vapour, in particular to hydrogen and ammonia, which are lighter than air.

We are indebted to the Colston Research Society of the University of Bristol for assistance in the purchase of apparatus.

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## LXXIII. *The Distribution of Electrons among Atomic Levels.*

By EDMUND C. STONER, B.A., *Emmanuel College, Cambridge* \*.

### 1. *Introduction.*

THE scheme for the distribution of electrons among the completed sub-levels in atoms proposed by Bohr† is based on somewhat arbitrary arguments as to symmetry requirements; it is also incomplete in that all the sub-levels

\* Communicated by R. H. Fowler, M.A.

† Bohr, *Zeit. f. Phys.* ix. p. 1 (1922); or 'The Theory of Spectra and Atomic Constitution,' Essay III. (Cambridge, 1922).

known to exist are not separately considered. It is here suggested that the number of electrons associated with a sub-level is connected with the inner quantum number characterizing it, such a connexion being strongly indicated by the term multiplicity observed for optical spectra. The distribution arrived at in this way necessitates no essential change in the process of atom-building pictured by Bohr; but the final result is somewhat different, in that a greater concentration of electrons in outer sub-groups is indicated, and the inner sub-groups are complete at an earlier stage. The available evidence as to the final distribution is discussed, and is not unfavourable to the scheme proposed.

## 2. Classification and number of X-ray Levels.

The X-ray atomic levels may be conveniently classified by means of three quantum numbers— $n$  (total),  $k$  (azimuthal), and  $j$  (inner), as shown in Table I.

TABLE I.—Classification of X-ray Levels.

[“Relativity doublet” terms are bracketed.]

Level .....	K	L			M				
Sub-level .....		$L_I$	$L_{II}$	$L_{III}$	$M_I$	$M_{II}$	$M_{III}$	$M_{IV}$	$M_V$
$n$ .....	1	2	2	2	3	3	3	3	3
$k$ .....	1	1	2	2	1	2	2	3	3
$j$ .....	1	1	1	2	1	1	2	2	3
Optical term ...	$1\sigma$	$2\sigma$	$2\pi_2$	$2\pi_1$	$3\sigma$	$3\pi_2$	$3\pi_1$	$3\delta_2$	$3\delta_1$

This classification has been put forward by Landé\*. In contradistinction to the older schemes, such as that of Sommerfeld, it gives a satisfactory selection principle ( $k$  changes by 1,  $j$  by 1 or 0), and at the same time brings out clearly the analogy between X-ray and optical spectra. The sub-levels may, in fact, be regarded as corresponding to typical  $\sigma$ ,  $\pi$ ,  $\delta$  ... doublet-series terms, as for alkali metal arc spectra, in the way indicated in the last row of the table.

The main criticism to be advanced against the classification

\* *Zeit. f. Phys.* xvi. p. 391 (1922).

is that it invalidates the interpretation of terms such as  $L_{II}-L_{III}$  as simple relativity doublets, although their separation is given accurately by Sommerfeld's formula. Bohr\*, however, has shown that though  $L_I-L_{III}$  was to be regarded as a relativity + screening doublet, the further subdivision into separate relativity ( $L_{II}-L_{III}$ ) and screening doublets ( $L_I-L_{II}$ ) was not justifiable. De Broglie and Dauvillier†, who adopt a scheme somewhat similar to the above, but with a larger number of sub-groups, point out that the "relativity doublet" separation increases in a similar way to that of the optical doublet with increase in atomic number. Landé, in two recent papers‡, has traced out the analogy in quantitative detail. He shows that the relativity and optical doublet separations can both be represented by the same general formula, and places beyond doubt that the two types of doublet are essentially similar in origin.

Now, observations on the anomalous Zeeman effect show that the optical doublets must have a magnetic origin; and although the magnetic explanations are as yet inadequate, it is justifiable to apply those ideas which have coordinated the optical data to the case of X-rays—in particular in the assignment of inner quantum numbers, as in the above scheme.

De Broglie and Dauvillier postulate a larger number of sub-levels (6M, 10N ...) in order to account for certain weak X-ray lines observed; the necessity for this, however, is not admitted by most workers, and it is undoubted that not more than 5M absorption discontinuities have been directly observed§. The work of Robinson|| on excited electrons, moreover, seems to prove conclusively that there are only 5M, and probably 7N, levels. The experiments thus support the view that for Röntgen spectra, as for optical doublet series, the number of sub-levels characterized by different  $j$ 's into which a given  $k$  level subdivides is restricted to two.

\* Bohr and Coster, *Zeit. f. Phys.* xii. p. 342 (1923).

† *Journ. de Phys.* VI. v. p. 1 (1924).

‡ *Zeit. f. Phys.* xxiv. p. 88 (1924) and xxv. p. 96 (1924).

§ Cf. Coster, *Phys. Rev.* xix. p. 20 (1922); Ross, *Phys. Rev.* xxii p. 221 (1923).

|| *Proc. Roy. Soc. civ.* p. 455 (1923).



## 3. Suggested Distribution of Electrons.

In the classification adopted, the remarkable feature emerges that the number of electrons in each completed level is equal to double the sum of the inner quantum numbers as assigned, there being in the K, L, M, N levels, when complete, 2, 8 ( $2 + 2 + 4$ ), 18 ( $2 + 2 + 4 + 4 + 6$ ), 32 ... electrons. It is suggested that the number of electrons associated with each sub-level separately is also equal to double the inner quantum number. The justification for this is discussed below. A summarized periodic table (Table II.) is given, which shows the nature of the distribution suggested. In the table the number of electrons in the sub-levels of the atom named on the left is given by the whole of the part of the table above and to the left of the thick line which begins under the atom. Krypton, for example, has 2K, 8L, 18M, and 8N electrons.

TABLE II.—Suggested Distribution of Electrons.

[The distribution of electrons in the atoms is given by the part of the table above and to the left of the thick lines]

Element.	Atomic Number.	Level ( <i>n</i> ).	Sub-Level. ( <i>k, j</i> )						
			I	II	III	IV	V	VI	VII
			1, 1	2, 1	2, 2	3, 2	3, 3	4, 3	4, 4
He .....	2	K (1)	2						
Ne .....	10	L (2)	2	2	4				
Ar .....	18	M (3)	2	2	4	(4)	(6)		
Kr .....	36	N (4)	2	2	4	(4)	(6)	(6)	(8)
Xe .....	54	O (5)	2	2	4	(4)	(6)		
Rn .....	86	P (6)	2	2	4				

## 4. Comparison with Bohr's Distribution.

A summarized Bohr's periodic table (Table III.) is given for purposes of comparison. This, and also Table II., should be referred to in conjunction with a more complete table. The Bohr distribution cannot be easily put in the form of Table II., owing to the way in which the sub-groups undergo further development after reaching a first pseudo-completeness; but the relation between the two tables will be obvious on inspection.

TABLE III.—Distribution of Electrons in Atoms, according to Bohr.

Element.	Atomic Number.	Sub-Levels. ( <i>n, k.</i> )															
		K		L		M			N				O				
		1	2	2	3	3	3	4	4	4	4	5	5	5	6	6	
		1	1	2	1	2	3	1	2	3	4	1	2	3	1	2	
He.....	2	2															
Ne.....	10	2	4	4													
A.....	18	2	4	4	(4 4)	→											
Kr.....	36	2	4	4	(6 6 6)	→	(4 4)										
Xe.....	54	2	4	4	6 6 6	→	(6 6 6)	→				(4 4)	→				
Nt.....	86	2	4	4	6 6 6	→	(8 8 8 8)	→	(6 6 6)	→		(6 6 6)	→	4	4		

It can be seen at once that the distribution proposed is equally in harmony with the essential features of the development process pictured by Bohr as his own; which means that it is equally in accord with chemical considerations which are so beautifully covered by Bohr's scheme, especially in its attribution of the similarity in chemical properties of such sequences as the rare earths to the development of underlying groups of electrons.

A question which arises is whether the Bohr ( $n, k$ ) levels are to be regarded as corresponding to the ( $n, k$ ) or the ( $n, j$ ) in the alternative scheme; for example, whether Bohr's (2, 1) level corresponds to  $L_I$  or  $L_I + L_{II}$ . The latter might seem reasonable in that (2, 2, 1) and (2, 1, 1) levels are more alike in certain respects, notably in energy

value, than  $(2, 2, 1)$  and  $(2, 2, 2)$ ; but the former is the direct and usual interpretation, and will be assumed here for the present. There is then a considerable difference in the assignment of electrons to  $(n, k)$  levels, the numbers running  $(2, 6)$ ,  $(2, 6, 10)$ , and  $(2, 6, 10, 14)$  for the L, M, and N  $(n, k)$  sub-groups in place of  $(4, 4)$ ,  $(6, 6, 6)$ , and  $(8, 8, 8, 8)$ . If, however, Bohr's  $(n, k)$ , for this purpose, should be taken to correspond with our  $(n, j)$  levels, the numbers to be compared with Bohr's are  $(4, 4)$ ,  $(4, 8, 6)$ , and  $(4, 8, 12, 8)$ .

As to the process of up-building, analogous sequences of elements correspond exactly on both schemes to analogous developments in the number and distribution of electrons; but the reorganization of underlying groups occurs in a much simpler manner in the scheme proposed. Beginning at Sc (21), 10 electrons complete the M group (noticeably beginning when there are 2, not 4, electrons in the N group); on our view these simply fill up the vacant  $(n 3, k 3)$  levels, precisely 10 electrons being required; on Bohr's view the change also involves addition of electrons to the inner sub-levels—in fact, a complete reorganization of the whole M group. The added electrons referred to are bracketed in Table II., and the corresponding development on Bohr's scheme is indicated by the arrow in Table III. A similar process, probably beginning at Y (39), occurs when the 10  $(n 4, k 3)$  electrons are added, and again, beginning at Lu (71), for the 10  $(n 5, k 3)$  electrons. The  $(n 4, k 4)$  level requires 14 electrons, and the adding of these corresponds to the rare earth sequence; on the Bohr view, a complete reorganization of the ~~M~~ group occurs. The dotted brackets and dotted arrow indicate this development.

The present scheme, then, accounts well for the chemical properties; it differs from Bohr's in the final distributions suggested, and in the fact that inner sub-groups are completed at an earlier stage, subsequent changes being made by simple addition of electrons to outer sub-levels without reorganization of the group as a whole.

### 5. *Significance of Inner Quantum Numbers.*

From a physical point of view, the real significance of inner quantum numbers, especially when applied to inner X-ray atomic levels, is very problematical. Evidence based on the analogous optical spectra, however, provides strong justification for the idea of the number of electrons

in a sub-group being related to the inner quantum number in the way assumed.

The case of the doublet series of the alkali methods only need be considered. In the atoms there is one electron external to a core composed of a completed system of electronic groups. Observations on the Zeeman effect can be correlated by assigning inner quantum numbers  $k$  and  $(k-1)$  to the atom with the electron in a  $k$  level. For  $\pi$  terms ( $k=2$ ),  $j=1$  or  $2$ , giving  $\pi_2$  and  $\pi_1$ ; for  $\delta$  terms ( $k=3$ ),  $j=2$  or  $3$ . There is actually a certain degree of arbitrariness as to the absolute value given to  $j$ ; for instance, values  $\frac{1}{2}$  and  $\frac{3}{2}$  for  $\pi_2$  and  $\pi_1$ ,  $\frac{3}{2}$  and  $\frac{5}{2}$  for  $\delta_2$  and  $\delta_1$  can be made to fit the facts equally well\*. This difficulty, however, is irrelevant, for the reason given below. The inner quantum number is usually interpreted as giving the magnetic moment of the atom as a whole, and the number of possible energy states of the atom in a weak external magnetic field, in which core and light electron are not separately affected, is attributed to the number of possible orientations of the atom in virtue of space-quantization.

The actual number of possibilities is given by the multiplicity of terms in the anomalous Zeeman effect, and can be deduced very straightforwardly (in simple cases at least) from observations on the behaviour of the lines. The point which it is desired to emphasize here is that, however the inner quantum numbers are interpreted, if they are given the values used above ( $k$  and  $k-1$ ), twice the inner quantum number does give the observed term multiplicity as revealed by the spectra in a weak magnetic field. (Thus in a weak magnetic field there are  $2\sigma$ ,  $2\pi_2$ , and  $4\pi_1$  terms.) In other words, the number of possible states of the (core + electron) system is equal to twice the inner quantum number, these  $2j$  states being always possible and equally probable, but only manifesting themselves separately in the presence of the external field.

At present it is not clear whether the number of equally probable states indicates that the atom as a whole is always the same as concerns relative orientation of core and outer electron orbit, and can take up  $2j$  different orientations relative to the (weak) field; or that the core takes up a definite orientation relative to the field, and the outer electron orbit can take up  $2j$  different orientations relative

\* For a fuller discussion of this whole subject, see Sommerfeld, 'Atombau und Spektrallinien,' and recent papers by Sommerfeld and Landé, e.g. Sommerfeld, *Ann. der Phys.* lxx. p. 32 (1923), lxxiii. p. 39 (1924); Landé, *Zeit. f. Phys.* xix. p. 112 (1921).

to the core\*. (The mutual influence becomes of less relative importance as the strength of the field increases, so that ultimately the field affects electron and core separately, and the Paschen-Back effect is obtained.) There may be some quite different interpretation.

The spectral term-values themselves, in so far as they are altered by external fields, would seem to depend primarily on the outer electron orbit itself (and not so much on electron + core, as do the magnetic properties of the atom); and remembering this, it seems reasonable to take  $2j$  as the number of possible equally probable orbits.

Without laying too much stress on any definite physical interpretation, or pressing the analogy too far, it may be suggested that for an inner sub-level, in a similar way, the number of possible orbits is equal to twice the inner quantum number, these orbits differing in their orientation relative to the atom as a whole. Electrons can enter a group until all the possible orbits are occupied, when the atom will possess a symmetrical structure.

That the inner quantum numbers are analogous to those for the alkali metals, is presumably connected with the fact that the building-up can always be regarded as occurring on a sub-structure of the inert gas atom type with completed group systems. The complicated optical multiplet series occur when there are light-electrons moving externally to incompleting groups.

In brief, then, it is suggested that, corresponding roughly to the definite indication in the optical case, the number of possible states of the atom is equal to  $2j$ ; so, for the X-ray sub-levels,  $2j$  gives the number of possible orbits differing in orientation relative to the atom as a whole; and that electrons can enter a sub-level until all the orbits are occupied.

#### 6. *Statistical Weight of Electrons bound in Atoms.*

If electrons in the atom are distributed according to the present scheme, the interesting point is suggested that all electrons bound in the atom forming constituents of completed groups are to be regarded as having the same statistical weight, namely unity (or  $h^3$ ); for there is then one electron in each possible equally probable state.

\* This general question and the allied one of the orientation of the inert gas atoms in a magnetic field are discussed by Bohr, *Ann. der Phys.* lxxi. p. 228 (1923).

## 7. Evidence as to Electron Distribution.

Unfortunately there are few properties which depend solely on the number of electrons in levels and not also on the type of level and its energy value; so that, in the present state of theory, a definite test of the merits of different distributions proposed is difficult. Some evidence, however, is available from which a few conclusions may be drawn; and the general lines of evidence on which the question must finally be decided are briefly considered.

## (a) Intensities of X-ray lines.

The intensity of X-ray lines will depend in part on the number of electrons in levels between which transitions occur; a simple relation between the relative numbers of electrons in two sub-levels and the relative intensities of the lines corresponding to transitions from these to the same final level would only be expected to hold when the sub-levels are close together, so that the energy associated with each transition is approximately the same, and when the sub-levels are of the same  $nk$  type. It has been shown for optical multiplets that the probability of possible transitions is not then dependent on the inner quantum number characterizing the terms concerned\*. In the optical case, however, the outer electron switches over to a lower level, and no disturbing factors enter owing to the presence of intervening electrons between the levels concerned. For the X-ray case, on the other hand, transitions occur between levels across intervening occupied electronic orbits, which may modify the probability of transition from different  $j$  types of  $k$  orbit.—Simple relations would only be expected for transitions between contiguous levels such as  $L \rightarrow K$ ,  $M \rightarrow L$ . A straightforward theoretical interpretation of observed relative intensities is thus only possible for a few cases.

From an experimental point of view, the relative intensity of different X-ray lines is difficult to determine, except when the lines are fairly close, so that corrections otherwise necessary, which cannot at present be accurately calculated, need not be applied. In one case very accurate measurements have been made, namely for  $K\alpha_1$  ( $L_{III} \rightarrow K$ ) and  $K\alpha_2$  ( $L_{II} \rightarrow K$ ). The results are as follows:—

	Fe.	Cu.	Zn.	Mo.	W.
$\alpha_2/\alpha_1$ .....	499	512	500	52	50

\* Ornstein and Burger, *Zeit. f. Phys.* xxiv. p. 41 (1924).

The first three, due to Siegbahn and Žáček\*, are the means of a large number of photometric measurements, agreeing closely among themselves; the last two, obtained from ionization measurements, are due to Duane and Patterson, and Duane and Stenström.

The ratio  $\alpha_1/\alpha_2$  is thus practically constant and equal to 2/1 from Fe (26) to W (74).

This result can at once be explained on the assumption that there are twice as many electrons in the  $L_{III}$  as in the  $L_{II}$  sub-level. Now, in Bohr's scheme four electrons are assigned to the (2, 2) level, so that 4 electrons have to be divided between  $L_{II}$  and  $L_{III}$ —a ratio 3/1 or 1/1 for the  $\alpha$  lines would be expected, certainly not 2/1.

For the  $L\beta$  group, Duane and Patterson† give for tungsten  $\beta_1, \beta_2, \beta_3, \beta_4$  as 100, 55, 15, 9. (See Table IV. for the transitions involved.) The  $\beta_3/\beta_4$  value again suggests the 2/1 ratio for the number of electrons assigned to the  $M_{III}$  and  $M_{II}$  sub-levels.  $\gamma_1, \gamma_2, \gamma_3, \gamma_4$  have relative intensities 100, 14, 18, 6.  $\gamma_2$  and  $\gamma_3$  correspond to transitions from N to L across the M group, and disturbing factors may come in, so that the  $\gamma_3/\gamma_2$  value is not inconsistent with a 2/1 electron ratio.

The importance of disturbances due to intervening electrons must be stressed; for it should be noted that the relative intensities of components of doublets such as  $\beta_3\beta_4$  and  $\gamma_2\gamma_3$  change considerably with the atomic number, even after all the levels directly concerned are completed, the two components approaching equality for high atomic numbers.

As to switches from the same initial level to different final L levels, Coster‡ states that “for all elements  $l$  is 2–3 times as strong as  $\eta$ , and  $\beta_6$  2–3 times as strong as  $\gamma_5$ ,” supporting the conclusion that  $L_{III}$  has twice as many electrons as  $L_{II}$  (so that it is twice as likely to lose an electron by ionization).

The very meagre results available as to line-intensities are practically exhausted in the above account; much further experimental (and theoretical) work is necessary. The results, however, do give definite support to the allocation of 2 electrons to the II sub-levels, and 4 to the III sub-levels, in the L, M, and probably N groups.

\* Data used, together with references to the original papers, will be found in Siegbahn, ‘Spektroskopie der Röntgenstrahlen’ (Berlin, 1924), pp. 96, 97, 106.

† Proc. Nat. Acad. Sci. vi. p. 518 (1920).

‡ Phil. Mag. xliii. p. 1088 (1922).

TABLE IV.—Showing Transitions corresponding to K and L lines.

Level (n) .....	K (1)			L (2)					M (3)					N (4)				
Sub-level .....				I	II	III			I	II	III	IV	V	I	II	III	IV	V
k, j .....	1, 1			1, 1	2, 1	2, 2			1, 1	2, 1	2, 2	3, 2	3, 3	1, 1	2, 1	2, 2	3, 2	3, 3
Number of Electrons...	2			2	2	4			2	2	4	4	6	2	2	4	4	6
K Series .....	K			$\alpha_3$ $\alpha_1$					$\beta_{3L}$ $\beta_1$					$\beta_2$				
L Series ...	$L_I$			$\beta_1$ $\beta_3$					$\gamma_2$ $\gamma_3$					$\gamma_1$				
.....	$L_{II}$			$\eta$					$\beta_1$					$\gamma_3$				
( $L_{III}$ )				$l$					$\alpha_2$ $\alpha_1$					$\beta_2$				



Two other matters concerned with X-ray lines may be briefly noticed. Firstly, new lines would be expected to appear for the same atomic number on both Bohr's and the present scheme, as they are exactly similar as regards points of origin of group development. Secondly, if the appearance of "anomalous" longer wave-length satellites to lines is connected with the development of the corresponding, or associated, sub-groups, it might be possible to decide whether development occurs simply by addition of electrons to outer sub-groups, or also by reorganization of inner sub-groups. Coster gives some examples, but the data are insufficient as yet to make further discussion useful; it may be mentioned, however, that no irregularities are observed at all for  $\beta_6$  and  $\gamma_5$  during the development of the N group.

(b) *Absorption of X-rays.*

The relative absorption of X-rays by different sub-groups of electrons, as the relative intensities of lines corresponding to switches from them, will depend in part on the number of electrons they contain. Theories of absorption, as yet very incomplete, indicate that the part  $\alpha_p$  of the characteristic atomic absorption due to a level P containing  $N_p$  electrons may be written :

$$\alpha_p = K\lambda^3 \frac{N_p}{f(n_p)},$$

where  $N_p$  is the corresponding total quantum number.

Kramers\* does not consider the relative absorption for different subgroups (*e.g.*  $L_I$ ,  $L_{II}$ ,  $L_{III}$ ), but gives as an approximate expression for the groups as wholes :

$$\alpha_p = K_1\lambda^3 \frac{N_p}{a_p n_p^3},$$

where  $a_p$  is the statistical weight of the electrons in the group. De Broglie†, semi-empirically, derives the expression :

$$\alpha_p = K_2\lambda^3 \frac{N_p}{\lambda_p^2},$$

$\lambda_p$  being the critical wave-length for the level concerned.

\* Kramers, Phil. Mag. xliv. p. 836 (1923).

† De Broglie, *Journ. de Phys.* VI. iii. p. 33 (1922).

As far as measurements on the relative K and L absorptions go, there is little to choose between the formulæ, though neither is adequate.

For orbits of a similar type, not too widely separated, it may, however, be anticipated that relative absorption, like relative emission, will depend primarily on relative numbers of electrons.

Owing to experimental difficulties, data as to relative absorption by different subgroups are meagre, Dauvillier's for gold being the only direct ones available \*. From his curves based on ionization measurements on absorption in the L region of Au, he deduces for the relative absorptions, for  $\lambda = \lambda_{L_I}$ :

$$(M + N + O \dots) : L_{III} : L_{II} : L_I = 42 : 62 : 41 : 35,$$

and applying de Broglie's expression, obtains

$$N_{L_{II}}/N_{L_{III}} = .495, \quad N_{L_I}/N_{L_{II}} = .78,$$

a conclusion which may be taken to support the 2, 2, 4 distribution of electrons.

In the M region, photographic methods only have been used. All that can be said is that the greater contrast corresponding to transitions from the outer sub-levels (see, for example, the photographs of Ross † for Th) suggests that they contain a greater number of electrons, as in the 2, 2, 4, 4, 6 distribution proposed.

The most powerful method of investigating the relative absorption by different subgroups, however, is by investigating the secondary corpuscular rays ejected from them, as in the work of Robinson ‡. Using homogeneous X-rays, the electrons emitted from a secondary radiator are bent round in a magnetic field, and fall on a photographic plate. The relative intensities of the lines (really heads of bands) corresponding to electrons from the different levels, when these are fairly close, give a rough estimate of the actual relative numbers of electrons ejected. Using copper K $\alpha$ -rays, Robinson gives the following visually estimated intensities (on a 1-6 scale) for the lines corresponding to

\* Dauvillier, *Comptes Rendus*, clxxviii. p. 476 (1924).

† Ross, *Phys. Rev.* xxii. p. 221 (1923).

‡ Robinson, *Proc. Roy. Soc. civ.* p. 455 (1923).

electrons ejected from the L sub-levels :—

	Ba.	I.	Sn.	Ag.	Mo.	Sr.	Cu.
L <sub>I</sub> .....	1	2	2	3	3	5	5
L <sub>II</sub> .....	1	3	3	4	4	5	
L <sub>III</sub> .....	6	6	5	5	5	5	5

The remarkable fact appears that the relative absorption by the different sub-levels varies with the difference between the critical wave-lengths and the incident wave-length in a manner quite unforeseen by any theories hitherto put forward. This is also observed by Ellis and Skinner\* with  $\gamma$ -rays. Over a wide range, however, in which the frequency is not too widely removed from the critical frequencies, and these themselves are not too close together, the run of intensities is exactly of the kind to be expected from a 2, 2, 4 distribution of electrons in the L subgroups; and in view of the strong evidence in favour of this distribution from other sources, it seems justifiable to consider the M intensities in a similar manner in the light of this. Robinson gives the following estimates :—

	Bi.	Pb.	Au.	W.	Ba.	I.	Sn.	Ag.
M <sub>I</sub> .....	1	1	1	1	4	5	4	5
M <sub>II</sub> .....	2	2	2	2	6	6	5	6
M <sub>III</sub> .....	5	5	5	5	6			
M <sub>IV</sub> .....	6	5	6	6	5	5	3	2
M <sub>V</sub> .....	6	6	6	6				

Here, again, the general run of the figures in the range in which, from the L results, anomalies would be least expected, is in accord with the 2, 2, 4, 4, 6 distribution. (The M<sub>I</sub>, M<sub>II</sub>, M<sub>III</sub> intensities show progressive change of the same type as the L<sub>I</sub>, L<sub>II</sub>, L<sub>III</sub>, as would be anticipated from their respective  $k_j$  values being the same.) The N sub-levels of bismuth give :

	N <sub>I</sub> .	N <sub>II</sub> .	N <sub>III</sub> .	N <sub>IV</sub> .	N <sub>V</sub> .	N <sub>VI</sub> .	N <sub>VII</sub> .
Bi .....	2	3	4	4	5	3-4	

Too much stress must not be placed on the evidence here brought forward as favouring the distribution proposed.

\* Ellis and Skinner, Proc. Roy. Soc. cv. p. 186 (1924).

The estimate of intensities is arbitrary, and it is difficult to say how far the estimated values correspond to actual numbers of ejected electrons\*. It has scarcely been sufficiently emphasized that the lines are really heads of bands; the number of electrons required is the total number in the band, and this number may diverge widely from that suggested by the line-intensity, particularly if the heads are close together. The inadequacy of theories of absorption, moreover, comes out most strongly in the very experimental results being considered. If, however, for sub-groups of similar energy relative absorption does depend largely on relative numbers of electrons under comparable conditions of excitation—and unless disturbing factors enter, it is difficult, physically, to imagine an alternative to this,—then the Robinson results do point definitely to a concentration of electrons in the outer sub-levels to an extent greater than it seems possible to account for on the basis of the Bohr numbers.

### (c) *Magnetic Properties.*

The ionic paramagnetism of the third-period elements only will be briefly considered here. The development of ions from  $K_+$  or  $Ca_{++}$  (with 18 electrons) to  $Cu_+$  (with 28 electrons) is brought about, on our view, by the simple addition of electrons to the  $M_{IV}$  and  $M_V$  sub-levels in 10 (4+6) orbits of the same  $nk$  type (3, 3).

Sommerfeld, taking into account spatial quantization, has shown† that the number of Bohr magnetons associated with the ions increases regularly by steps of 1 from 0 to 5 (attaining this maximum value for  $Mn_{++}$  and  $Fe_{+++}$  with 23 electrons), and then decreases regularly to 0 (for  $Cu_+$ ) with increasing numbers of electrons.

While the deeper meaning of this may be obscure, especially in that unit magnetic moment has apparently to be associated with (3, 3) orbits, such a beautiful regularity is in agreement with the development of the M group by the simple addition of 10 similar ( $n, k$ ) orbits; the presence of  $x$  electrons in the ( $M_{IV}$  and  $M_V$ ) levels, superposed on completed groups, may be expected (by a sort of Babinet principle!) to produce the same paramagnetic properties as  $(10-x)$  electrons, for with the latter number the group diverges from non-paramagnetic completeness in the absence of  $x$  electrons. On the Bohr scheme, the

\* Robinson discusses this question, *l. c.* p. 473.

† Sommerfeld, *Zeit. f. Phys.* xix. p. 221 (1923).

development occurs by a complete reorganization of the whole M group from a (4, 4) to a (6, 6, 6) arrangement. While the general nature of the change might be the same, the essential and striking feature—the regularity—would certainly not be anticipated.

(d) *Chemical Properties.*

Chemical properties depend mainly on the number of electrons in outer I, II, III sub-groups. The distribution proposed is primarily concerned with completed groups rather than their course of development; but a few rather suggestive features of the new scheme, where it diverges from Bohr's, may be mentioned. The course of development strongly indicated for the L (Li-Ne), M (Na-A), N (Cu-Kr), O (Ag-Xe), P (Au-Nt) sub-groups is shown in Table V.

TABLE V.—Number of Electrons in Outer Sub-groups.

Outer Sub-Group.	Column of Periodic Table and Typical Element.							
	I	II	III	IV	V	VI	VII	VIII
	Na	Mg	Al	Si	P	S	Cl	A
I	1	2	2	2	2	2	2	2
II			1	2	2	2	2	2
III					1	2	3	4

A consideration of the electrovalency of the elements as indicated by the halides, for example, provides considerable evidence for a subdivision of electrons among the levels in this way. Thus P is 5-valent, corresponding to all the five outer electrons in  $\text{PCl}_5$ , but also trivalent in  $\text{PCl}_3$ , corresponding to the three more loosely-bound ( $M_{II} + M_{III}$ ) electrons. (Similarly, the analogous Sb.) S forms  $\text{SF}_6$ ,  $\text{SCl}_4$ , and  $\text{SCl}_2$ . (There are analogous Se and Te compounds.) Si and the analogues C, Ge, Sn, Pb all form tetrachlorides, and Sn and Pb dichlorides. I forms  $\text{ICl}_3$  and  $\text{IF}_5$ , and also compounds in which it acts as heptavalent.

The development of underlying groups occurring from Sc-Ni, Y-Pd, and Lu-Pt involves the addition of 4 and 6 electrons in IV and V sub-groups. (See Table III.) The problem of coordination compounds and "residual affinity" is undoubtedly linked up with these underlying groups, and in this connexion the prevalence of 6 as the number of groups surrounding the central atom in the ion of many complex compounds seems very significant as indicating 6 as the number of electrons to be associated with the outermost of the underlying sub-groups (V) when completed. As examples may be given the cyanides such as  $H_4[Fe(CN)_6]$ ,  $H_4[Ru(CN)_6]$ ,  $H_4[Os(CN)_6]$ , and the ammines such as  $[Co(NH_3)_6]Cl_3$ ,  $[Pt(NH_3)_6]Cl_4$ . The number 6 also occurs in the Bohr scheme in a somewhat similar manner, and the chemical evidence has already been discussed in this connexion\*.

It seems undesirable here to enter more fully into chemical considerations, though they raise many important questions. The evidence is favourable, and the scheme seems to possess some new inherent possibilities for co-ordinating chemical facts.

A final remark may be made on the question of atomic symmetry as exemplified in carbon. According to Bohr, carbon has 4 (2, 1) electrons, whose orbits are taken to be tetrahedrally arranged. On the present view there are 2 (2, 1) and 2 (2, 2) electrons. The tetrahedral symmetry, therefore, is probably not to be attributed to the four outer electrons the atom possesses, but to the four "vacant places" which would have to be filled up for it to attain a complete configuration. Somewhat similar considerations may apply to the six-fold symmetry characteristic of coordination compounds of the type referred to above.

#### (e) Optical Spectra.

The relation between optical spectra and distribution of outer electrons has been (and is being) very fully considered by Bohr himself and others. Here it is only necessary to note the relevant fact that the doublet spectrum of ionized carbon (C II) † can at once be explained if  $C_+$  has 2 (2, 1) electrons and 1 (2, 2); whereas it cannot be fitted easily into a 4 (2, 1) scheme for neutral carbon. The spectra of silicon in various stages of ionization fit in with the scheme proposed, as also the recently analysed oxygen spectrum ‡.

\* Sidgwick, Journ. Chem. Soc. cxviii. p. 725 (1923).

† Fowler, Proc. Roy. Soc. cv. p. 299 (1924).

‡ Hopfield, Phys. Rev. xxi. p. 710 (1923).

### 736 *Distribution of Electrons among Atomic Levels.*

The correlation of the types of spectra with electronic structure, however, presents many unsolved problems for the future.

This section may be briefly summarized. The X-ray emission-line intensities seem to provide conclusive evidence for the presence of 2 and 4 electrons in  $L_{II}$  and  $L_{III}$  as inner atomic sub-levels over a wide range of atomic numbers, a subdivision also indicated for  $M_{II}$  and  $M_{III}$ . The absorption measurements confirm this, and suggest a distribution of the 2, 2, 4, 4, 6 type for the 5M and the first 5N sub-levels. The chemical evidence is strongly in support of the up-building of the I, II, III L, M, ... P sub-levels as suggested by the final 2, 2, 4 distribution, and this is confirmed in an important case by the optical spectra. The chemical properties also indicate strongly the number 6 as characterizing the M, N, and O V sub-groups, and magnetic considerations suggest 10 as the number of electrons in the completed  $M_{IV}$  and  $M_V$  sub-levels.

While evidence based on experiment is inadequate to provide quantitative proof of the correctness of the whole system of electronic distribution proposed, it seems conclusive as to the simpler sub-groupings, and collectively does lend strong support to a scheme in itself simple and consistent.

#### *Summary.*

A distribution of electrons in the atom is proposed, according to which the number in a sub-group is simply related to the inner quantum number characterizing it. A formal justification of the connexion is given. The suggested numbers of electrons in the sub-levels of the completed K, L, M ... groups are (2), (2, 2, 4), (2, 2, 4, 4, 6) ... respectively. The scheme is compared with that of Bohr. It enables all the essential features involved in Bohr's picture of atom-building to be retained, and so is equally in accord with general chemical and spectroscopic evidence; but it differs in the distribution in the completed groups, and in indicating a somewhat simpler mode of development. Evidence based on considerations of intensities of X-ray lines, absorption of X-rays, chemical and magnetic properties, and optical spectra is discussed and shown to give considerable support to a distribution of the kind put forward.

I would like to thank Mr. R. H. Fowler for helpful criticism and discussion.

Cavendish Laboratory,  
July 1924.

LXXIV. *A Suggestion as to the Structure of Light.*

By Sir J. J. THOMSON, O.M.\*

ONE of the most interesting facts in the history of the physical sciences is the contradiction between the evidence as to the nature of light afforded by its optical properties on the one side and its electrical ones on the other. There has perhaps never been a case where the agreement between the predictions of theory and the results of the most searching and accurate experiments has been so complete as in the undulatory theory of light—a theory which supposes that the disturbance which constitutes light is represented by a continuous function of the time and spatial coordinates and that the energy is distributed continuously throughout the beam. On the other hand, when we consider the electrical properties of light, everything points to great concentration of energy into discrete centres, and that “the front of a wave instead of being as it were uniformly illuminated is represented by a series of bright specks on a dark ground.”

Fig. 1.



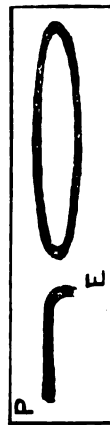
Fig. 2.



Fig. 3.



Fig. 4.



The electrical properties point just as clearly to something resembling the Newtonian corpuscular theory as the optical ones do to the undulatory theory.

I have for a long time used a mental picture, based on the idea of tubes of electric force, which I have found useful in reconciling the optics with the electricity.

On this view the mutual potential energy of an electron *E*

\* Communicated by the Author.



and a positive charge  $P$  is located in the tube of force stretching between  $E$  and  $P$ . If the electron falls from  $E$  to  $E'$  this potential energy is diminished by the energy in the portion  $EE'$  of this tube of force; for the energy in this portion to get free and travel out as light, the piece  $EE'$  of the tube must get into a state where it can travel freely with the velocity of light and not be associated with a charge of electricity whether positive or negative.

We may picture the energy as getting free in the following way : during the approach of  $E$  to  $P$  the tube  $EP$  may first be thrown into a loop as in fig. 2; the two sides of the loop near  $E'$  approach each other as in fig. 3; the closed part of the loop gets detached (fig. 4) and goes off as a closed ring, which rapidly becomes circular and travels with the velocity of light in a direction at right angles to its plane, like a circular vortex ring. The energy in the ring, which is that due to the fall from  $E$  to  $E'$ , remains constant as long

Fig. 5.



Fig. 6.



Fig. 7.

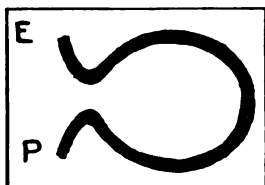
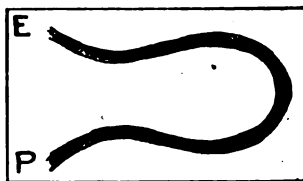


Fig. 8.



as the ring is unbroken. The emission of this ring is taken to represent the emission of radiation, and the energy of the light is concentrated in this ring.

For this ring to give up its energy a process the reverse of that which led to its formation has to be gone through. When the ring comes near a tube of force joining an electron to a positive charge, the stages indicated in the figs. 5, 6, 7, and 8 are gone through. When in the reverse

process the ring breaks and its tube of force gets attached to the electron in the stage represented in fig. 7, the energy in the circuit between P and E introduced by the ring is available for pulling the electron further away from P. If this energy is large enough to detach the electron from P, a free electron is produced and the ring disappears.

This will also be the case if the energy, though not sufficient to detach the electron altogether from P, is large enough to bring it into another position of equilibrium. Thus, suppose the electron were one in the second shell of electrons counting from the outside, there would be a position of equilibrium in the outer layer, and the energy of the ring would be spent in moving the electron from the second shell to the first, the ring would be destroyed, and there would be an absorption of energy. After a time the electron would fall from the first shell to the second, and emit the characteristic radiation by the processes indicated in figs. 2, 3, and 4. If, however, the energy in the ring were not sufficient to move the electron into a new position of equilibrium, then, though the absorption of the ring would make the electron start away from P, the forces acting upon it would soon stop it, and the motion would be reversed and the tube retrace its steps; the ring would be re-formed and break away from the molecule against which it struck, and in this case there would be no absorption.

Thus we see that the death of a ring means either the birth of a high-speed electron or the emission of a unit of characteristic radiation. This is in exact accordance with the exceedingly interesting and suggestive result obtained by Barkla, that when a beam of Röntgen rays is wholly absorbed in a gas without the emission of characteristic radiation, the number of high-speed electrons produced is independent of the kind of gas and its physical condition.

The rings are the centres in which the energy of light or Röntgen rays is concentrated. Any transference of energy from light to matter involves the destruction of these rings; thus the amount of energy transferred from a beam of monochromatic light or homogeneous Röntgen radiation must be an integral multiple of a unit.

#### *Energy of a Ring.*

If  $f$  is the electric polarization in the ring, the energy  $E$  is given by the equation

$$\begin{aligned} E &= 2\pi \times f^2 \times (\text{volume of ring}) \\ &= 2\pi \times f^2 \times \omega \times 2\pi r, \end{aligned}$$

where  $\omega$  is the cross-section of the ring and  $2\pi r$  its circumference. As the tube of force came from an electron  $\omega = pe$ , where  $e$  is the charge on an electron and  $p$  a number not greater than unity,  $p$  would be equal to unity if all the lines of force from the electron were done up into one bundle; it will have a smaller value if there are more bundles than one. Substituting this value for  $f$  and writing  $\omega = \pi b^2$ , where  $b$  is the radius of the cross-section of the ring, we find

$$E = 8\pi^2 p^2 e^2 \frac{1}{b^2} \frac{1}{2\pi r}.$$

Thus, if the rings are geometrically similar, their energy will be inversely proportional to their linear dimensions.

### *Waves round the Ring.*

At the time the ring is emitted from the atom, and indeed for some time before and after, the electric field in the atom is changing rapidly. This change will produce vibrations in the ring and give rise to electrical waves, so that before and after the ejection of the ring, electric waves are coming out of the atom; as these, like the ring, travel with the velocity of light, the ring will be the centre of a system of electrical waves of the normal type, and predominant among these are those which have the same periodicity as the vibrations of the ring. The energy in these waves will be small compared with that in the ring, because the total loss of energy by the atom is not far from the difference between the potential energy of the electrons in the positions  $E$  and  $E'$ .

We pass on now to consider whether this conception of the structure of light affords material for explaining interference and analogous phenomena.

We begin by remarking that the direction of motion of a free tube of force is at right angles to both the electric and magnetic forces, so that the direction of motion of such tubes may be altered by external electric and magnetic fields. As the ring is such a tube, the direction along which it moves can be deflected by applying electric or magnetic forces.

We suppose that when the ring is moving freely at right angles to its plane, it is surrounded and has travelling with it a distribution of electric force corresponding to a system of electrical waves of the ordinary type, diverging from the atom or molecule from which the ring was emitted. The distribution of electric force is periodic, and the period is

a period of vibration of the core about its circular configuration. If the waves surrounding the ring fall on a narrow slit in a metal plate parallel to the plane of the ring, the electric and magnetic forces in the parts of the wave in the slit are much greater than they were before the wave reached the slit. The directions of these forces change as well as their intensities, so that the Poynting vector, *i.e.* the direction of the flow of energy, will change in direction from place to place in the neighbourhood of the slit. Thus the flow of energy gets diverted when the wave passes through the slit; it is no longer always in one direction, but spreads out fanwise after leaving the slit. The result of this spreading is shown by the ordinary theory of diffraction to lead to such a distribution of energy in the electrical waves after they have passed through the slit, that the density of energy travelling in a direction making an angle  $\theta$  with the normal is proportional to  $\sin^2 m\theta / (m\theta)^2$ , where  $m$  is a constant depending on the wave-length of the light and the width of the slit. The energy-path for a particular piece of energy will depend upon the part of the slit through which that energy passes.

As the ring is a tube of force, its path will be affected by the changes produced by the slit in the electric and magnetic force in the waves enveloping the ring. Since the ring is closed, it will give rise to but very small external magnetic and electric force; thus at places on a surface surrounding the ring and but a little way from it the electric and magnetic forces, and therefore the Poynting vector, will not be affected by the presence of the ring. We shall suppose that the path of the energy of the ring is the same as the path of the energy in the wave in its immediate neighbourhood. The angle through which the path of the energy is deflected will depend upon the part of the slit through which the ring passes. As the dimensions of the ring will in general be very small compared with the width of the slit, the ring is as likely to pass through one part of the slit as another; hence when a very large number of these rings pass through the slit, the flow of energy will be uniform throughout the slit, and the energy sent in any direction  $\theta$  will be proportional to that sent in the same direction by a plane continuous electric wave travelling horizontally towards the slit—*i.e.*, it will be proportional to  $\sin^2 m\theta / (m\theta)^2$ . Thus on these assumptions the diffraction patterns will be the same when the energy of the light is concentrated in a ring as when it is, as in the ordinary theory, spread throughout the whole of the wave. We can

apply the same considerations to explain the other interference effects, such as Fresnel's mirrors and the scattering of light and Röntgen rays by the molecules of a gas.

To sum up, light on this view is made up of units, each of which contains a core in which the energy is concentrated ; this core is surrounded by a system of electric waves which, though they have but little energy, give rise in cases where diffraction or interference occurs to electric and magnetic forces which deflect the paths of the cores without altering their energy. The core is supposed to vibrate in a definite period, and this period coincides with that of the electrical waves which surround it.

*Planck's Law.*

There ought on this law to be a very simple relation between the energy of the ring and the frequency of the light of which it is the unit. If  $E$  is the energy and  $\nu$  the frequency,

$$E = h\nu$$

where  $h$  is Planck's constant  $6.55 \times 10^{-27}$ .

Thus the frequency of the light is directly, and the wave-length inversely, proportional to the energy. This kind of relation might be expected on the view we are discussing, for we have seen that the energy of the ring is equal to

$$8\pi^2 \rho^2 v^2 \frac{r^2}{b^2 2\pi r} \dots \dots \dots (1)$$

If the rings are geometrically similar,  $r/b$  will be the same for all rings. The frequency of the waves is the same as that of the ring ; in geometrically similar rings we should expect the wave-length of the vibration to be proportional to the linear dimension. Hence from (1) we should expect the energy to be inversely proportional to the wave-length ; this is Planck's law. To estimate whether the value of the constant would be anything like Planck's value : let us suppose that the time of vibration of the ring is the time taken by light to travel round the circumference of the core ; then  $\nu = c/2\pi r$ , where  $c$  is the velocity of light. Hence from (1)

$$E = 8\pi^2 \rho^2 v^2 c^2 \frac{r^2 \nu}{b^2 c},$$

$$c = 4.8 \times 10^{10},$$

$$c = 3 \times 10^{10},$$

$$E = 6.2 \times 10^{-28} \frac{\rho^2 v^2}{b} \dots \nu.$$

So that if  $pr/h=\pi$ , the numerical value of the constant connecting  $E$  and  $\nu$  would agree well with Planck's value.

### *Absorption of Light.*

Absorption of light on this view involves the rupture of the rings forming the cores; the endless ring has to be broken, and, as its end cannot be free, they must join on to another tube of force connecting electrons and positive charges, the energy in the ring being communicated to the carriers of those charges. We have seen that for the ring to be permanently destroyed, the energy in the ring must be sufficient to produce some quasi-permanent change in the molecule, such as the ejection of an electron, or the movement of an electron from one position of equilibrium to another; if no such change is possible, the substance cannot take any energy from the light, and so will be quite transparent. Apart from selective absorption and resonance, which requires special treatment, the transparency of many substances to light in the visible or infra-red spectrum is very high; thus, for example, the light that reaches us from the sun and stars has passed through matter equivalent in mass to a layer of mercury 30 inches thick. On the other hand, ultra-violet light of very small wave-length, as in Schumann rays, may be absorbed by a layer of gas a few millimetres thick at a low pressure, and this effect seems too general to be altogether selective. The energy in each unit of light of this character, say of wave-length 1000 Å, is that corresponding to about 12 volts, which is of the order of the ionizing potential of gases; thus units of light of this kind have enough energy to produce a very definite chemical change in the molecule, and so would be liable to be absorbed.

Several factors have to be taken into consideration with regard to absorption. First the energy in the unit. An increase in this may enable the unit to effect certain changes, such as the expulsion of an electron or the removal of an electron from one layer to another, and thus increase the absorption. X When the energy in the unit is sufficient to produce all possible permanent or quasi-permanent changes in the disposition of the electron, any further increase in the energy is not likely to lead to an increase in the absorption. X When the unit has enough energy to be absorbed, the amount of absorption will depend upon the number of electrons hit by the ring as it passes through the absorbing substance; this number will depend upon the size of the ring. X Now, as we have seen, the radius of the ring is

inversely proportional to the energy, so that with an increase in energy the radius of the ring diminishes. Thus the effect of an increase in energy will be twofold ; it may increase the probability of a unit being absorbed if it makes a collision, but it diminishes the probability of the collision. When the energy in the ring is far greater than that corresponding to the ionizing potential of the gas, the second effect will be the more important, and the absorption will diminish as the size of the ring diminishes—*i.e.*, as the energy increases. On the other hand, when the energy in the ring sinks below that required for ionization complete or partial, the absorption will vanish ; hence at this stage there should be an enormous increase in absorption as the energy increases through a critical value—the absorption will reach a maximum and then diminish whether the energy increases or diminishes. X

Knowing the dimensions of the ring, the distance it must travel before meeting with an electron can be calculated without difficulty. We must remember, however, that a ring may meet an electron without suffering disruption, for it is only when the tube of force attached to the electron has the proper orientation with respect to the core that the process indicated in figs. 5, 6, 7, and 8 can take place, so that it is only a small fraction of the number of collisions between the rings and electrons which lead to disruption and therefore to absorption.

From these principles we can calculate the coefficient of absorption of light ; for if  $1/\lambda$  is the value of this coefficient,  $\lambda$  is the average distance travelled by a light-core before it is destroyed and its energy spent in increasing either the kinetic or potential energy of an electron. If  $A$  is the area of the cross-section of the light-core made by a plane through its centre and at right angles to the direction in which the ring is moving, and  $n$  the number per unit volume of electrons of the type of those which are to be detached or permanently displaced by the ring, the number of such electrons struck by the ring when it passes over a distance  $x$  is equal to  $A\lambda n$ . In order that the electron should be detached, it is not sufficient for it to be struck by the ring ; it must be struck when the tube of force attached to the electron is directed so that the processes shown in figs. 5, 6, 7, and 8 can occur. This tube must point in a particular direction, or rather it must be included in a cone of small angle. If  $\alpha$  is the semi-vertical angle of this cone, then if the orientation of the tube is not affected by the ring, the chance that the tube should point in the proper direction is  $\sin^2 \frac{\alpha}{2}$ . Thus, if

the ring were to move through a distance  $x$ , the number of times it would have met with an electron which would have broken it up is  $xAn \sin^2 \frac{\alpha}{2}$ ; hence  $\lambda$ , the average distance a ring travels before being destroyed, is given by the equation

$$\lambda = \frac{1}{An \sin^2 \frac{\alpha}{2}},$$

and the chance of the ring travelling a distance  $x$  without being absorbed is  $e^{-x/\lambda}$ . The minimum value of  $\lambda$  is  $1/An$  and the maximum value of the coefficient of absorption  $An$ . For the absorption to be as great as this, every electron when struck by the ring must have its tube of force pointing in the right direction: for this to be the case the direction of these tubes of force must be determined by the light wave itself.

### Resonance.

The effect of resonance on this theory is due to the effect of the light on the orientation of the tubes of force attached to the electrons. Suppose that the period of the light is the same as that of the electron which is to absorb the energy of the ring; then the waves preceding the ring having the same period as this electron will have a great effect upon it and will make the tube of force attached to it tend to point in a definite direction. Thus, when the ring strikes the electron, the tube of force attached to the electron, instead of being as likely to point in one direction as in any other, will be concentrated along a definite direction, so that the probability of the rupture of the ring will not be the same as when there is no resonance. If the directions of the electron tubes were all brought by the resonance effect into the position for the rupture of the ring, the free path of the ring would be  $1/An$  instead of  $1/An \sin^2 \frac{\alpha}{2}$ , and the coefficient of absorption would be  $An$ ; hence a slower limit to  $An$  would be the coefficient of absorption of the light. The only value for such a coefficient I have been able to find is one given by Professor R. W. Wood (Phil. Mag. xxiii. p. 696, 1912), who found that the intensity of the mercury line 2536 was reduced to half its value by passing through 5 mm. of mercury vapour at a pressure of .001 mm.

Hence, if  $a$  is the coefficient of absorption,

$$a = 2 \log_e 2 = 1.4.$$



The number of atoms of mercury in 1 c.c. at a pressure of .001 mm. at  $0^{\circ}\text{C}$  is  $3.6 \times 10^{13}$ .

The electrons concerned with light of this wave-length are those of the outer layer. We shall suppose that there are two such electrons per atom; hence  $n = 7 \times 10^{13}$ . The lower limit of  $A$  is given by the equation

$$An = a \quad \text{or} \\ 7 \times 10^{13} A = 1.4;$$

hence the lower limit of  $A$  is  $2 \times 10^{-14}$ . This is considerably greater than the area of a circle whose radius is that of the atom; as the ring is an anchor-ring with a hole in the middle, the radius of the ring forming the core of light of this wave-length must be much larger than  $10^{-8}$ . So that the rings for light of this quality must be large compared with atoms.

The mass of a ring is equal to  $2h/c\lambda$ , where  $h$  is Planck's constant  $6.55 \times 10^{-27}$ ,  $c$  the velocity of light  $3 \times 10^{10}$ , and  $\lambda$  the wave-length. Even when the wave-length is as small as the radius of an atom, this mass is very small compared with that of an electron  $8.8 \times 10^{-28}$ ; so that in a collision between an electron and a ring there would be very little transference of energy, though the effect on the direction of motion of the ring might be considerable.

On the view we have taken, the production of a ring is due to a deformation in the tubes of electric force produced by a rapid diminution in the potential energy. It is possible to imagine electric waves without a ring; thus, if an electron is moved with uniform velocity round the circumference of a circle with a positive charge at its centre, electric waves whose frequency is that of the moving electron will be generated, but will not necessarily be accompanied by a ring.

LXXV. *On the Relation between Metal Contact Potentials and the Peltier Effect.* By J. A. V. BUTLER, M.Sc., University College of Swansea\*.

THE electromotive force in a closed circuit of two metals A and B with junctions at the temperatures  $T_1$  and  $T_2$  may be expressed by either of the following equations:—

$$e = E_1 - E_2 + \int_{T_1}^{T_2} (\rho_a - \rho_b) dT, \quad \dots \quad (1)$$

$$e = q_1 - q_2 + \int_{T_1}^{T_2} (\sigma_a - \sigma_b) dT, \quad \dots \quad (2).$$

\* Communicated by the Author.

where

$e$  = e.m.f. of the whole circuit.

$E_1, E_2$  = contact P.D.'s at the junctions at  $T_1, T_2$  respectively.

$q_1, q_2$  = corresponding reversible heat effects at the junctions. (Peltier coefficients.)

$\rho_a, \rho_b$  = P.D.'s in the two metals A and B for unit difference of temperature.

$\sigma_a, \sigma_b$  = corresponding Thomson coefficients, i.e., reversible heat effects in passage of unit quantity of electricity through unit difference of temperature.

The first equation expresses the fact that the e.m.f. round the circuit is the sum of the individual P.D.'s; the second is an expression of the first law of thermodynamics as applied to the thermoelectric circuit which demands that the heat absorbed in the Peltier and Thomson effects shall be equal to the Joulian heat evolution in the whole circuit,  $e$  per unit quantity of electricity. The similarity between (1) and (2) has led to their frequent identification term by term, and the confusion which has resulted has persisted in text-books and original papers to the present time.

Apart from this confusion of thought the numerical correspondence of  $E$  and  $q$  has been very strenuously maintained. Sir Oliver Lodge, at one time the champion of this view\*, vigorously maintained that "The total contact force at any junction can be experimentally determined by measuring the reversible energy developed or absorbed there per unit quantity of electricity conveyed across the junction."

Now the reversible heat evolution at a junction is equivalent to a few millivolts at the most. Those who took the view that this was the whole electromotive force at the junction were bound to ascribe the much greater Volta potential to other effects, e.g., to "chemical action" in the system A/air/B†.

In more recent times overwhelming evidence has accumulated which makes it impossible to doubt the existence of a real contact difference of potential between two metals of a much greater order of magnitude than the Peltier effect. It is demanded by the theory of electron emission from metals‡; it has been experimentally demonstrated in a

\* Phil. Mag. [5] vol. xix. (1885); B. A. Reports, Montreal, 1884.

† Lodge, *loc. cit.*; also Phil. Mag. vol. xlix. p. 351 (1900), Proc. Phys. Soc. Lond. vol. xvii. p. 369 (1900).

‡ Cf. Richardson, 'Emission of Electrons from Hot Bodies.'

particularly conclusive and elegant manner by Millikan and his co-workers \*.

What, then, is the relation between the Peltier heat effect and a junction and the real contact P.D.?

We shall endeavour to give a fairly complete answer to this question by developing the statistical theory of metal boundary potentials, the results of which will be shown to be entirely in accordance with the requirements of the laws of thermodynamics.

It can be shown †, by means of a thermodynamical argument (and indeed is obvious if the matter is viewed rightly), that if  $w_a$  and  $w_b$  are the latent heats of evaporation of electrons from the two metals and therefore  $w_a - w_b$  is the total energy change in the transfer of an electron from A to B, that

$$E - \frac{w_a - w_b}{F} = q, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now rewriting (1) and (2) in the differential forms

$$de = dE + (\rho_a - \rho_b) dT, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$de = dq + (\sigma_a - \sigma_b) dT, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and applying the second law of thermodynamics to the reversible heat effects by means of the equation

$$d(q/T) = - \frac{\sigma_a - \sigma_b}{T} dT,$$

we obtain the well-known Kelvin equation

$$q = T \frac{de}{dT}, \quad . \quad . \quad . \quad . \quad . \quad (5A)$$

and introducing this value of  $q$  into (3), we find

$$E - \frac{w_a - w_b}{F} = T \frac{de}{dT}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

an equation which resembles the well-known Gibbs-Helmholtz equation for the whole of a galvanic cell,

$$\epsilon - \frac{U}{nF} = T \frac{d\epsilon}{dT},$$

but differs in that in (6)  $e$  refers to the whole circuit whereas  $E$  refers only to one junction.

The relation between contact potentials and the Peltier

\* Phys. Rev. vol. vii. p. 18 (1916); vol. xviii. p. 236 (1921).

† Richardson, 'Electron Theory of Matter,' 1916, p. 455.

effect has also been investigated by Lord Kelvin \*, who made use of a very ingenious thermodynamical engine and obtained the equation

$$\frac{dV}{dt} = Q/t,$$

where  $V$  = Volta P.D. at junction.

$Q$  = sum of Peltier effect at junction and "quasi-Peltier effects" if any at air or other metal surfaces.

The matter cannot be pushed any further on these lines because it is not possible to treat thermodynamically the behaviour of a single junction, *i.e.*, without introducing a return path. In order to elucidate it further it is necessary to turn to statistical considerations.

*Statistical Theory of Metal Boundary Potentials.*

*Case (a).*—Consider a single metal in a closed space containing an electron atmosphere of concentration electrons per unit volume, all at the temperature  $T$ . The rate at which unit area of the metal loses electrons at this temperature when uncharged is given by the ordinary thermionic expression. The rate at which electrons are deposited from the atmosphere is  $n\sqrt{T/2\pi m}$ . If the rate of loss is greater than the gain, the metal will acquire a positive charge which will accumulate until a state of balance is reached. Let the surface P.D. corresponding to the work done against this charge by an electron in escaping be  $E$ . The work which an electron must do before escaping from the metal is now  $W_1 - EF$  and the condition of equilibrium is

$$k_1\sqrt{T}e^{-\frac{w_1 + EF}{RT}} = n\sqrt{T/2\pi m}, \quad \dots \quad (7)$$

(assuming that the electron concentration is not markedly affected in attaining equilibrium);

$$\therefore E = -\frac{w_1}{F} - \frac{RT}{F} \log_e n - \frac{RT}{F} \log_e K. \quad \dots \quad (8).$$

The potential difference at the surface of a metal therefore depends on the concentration of the electron atmosphere and varies logarithmically with it.

*Case (b).*—Now consider the case of two metals in the electron atmosphere together but not in contact. Equilibrium at the surface of each will be conditioned as in Case (a) and equilibrium will be represented by the equations

$$k_1\sqrt{T}e^{-\frac{w_1 + E_1 F}{RT}} = n\sqrt{T/2\pi m},$$

$$k_2\sqrt{T}e^{-\frac{w_2 + E_2 F}{RT}} = n\sqrt{T/2\pi m},$$

\* Collected Works, vol. v. p. 20; Phil. Mag. vol. xlv. p. 82 (1898)

whence 
$$E_1 - E_2 = \frac{w_2 - w_1}{F} + \frac{RT}{F} \log_e \frac{k_1}{k_2} \quad (9)$$

That is, although the surface P.D. of both metals is dependent on the electron atmosphere concentration, the difference for any two metals is characteristic of them, therefore their intrinsic P.D.

*Case (c).*—We can now consider the case of two metals in contact. It can be said at once that the conditions at the surfaces not in contact are unaltered, that when equilibrium is attained electrons arrive at and escape from every portion of the metals at equal rates. Otherwise a continuous flow of electricity across the junction would be necessary to redress the balance, and a heat absorption or evolution at the junction by the Peltier effect would occur which would violate the second law of thermodynamics. There must therefore be a P.D. at the metal junction equal to the intrinsic P.D. of the metals, and at equilibrium equal numbers of electrons must pass the junction between the metals in both directions in the same time.

Before an electron can escape from either metal into the other, it will have to perform a certain amount of work. This may not be identical with the thermionic work function  $w_1$  or  $w_2$ ; the forces of attraction exerted on an electron by the metals on either side of the junction may overlap to some extent, but the work done against these forces in the transfer of an electron from the interior of the first to the interior of the second metal must always be  $w_1 - w_2$ . Let the amounts of work against these attractive forces to be done in escaping across the boundary from the metal on either hand be  $w_1'$  and  $w_2'$ . The rates of escape before any electric forces are set up will be  $k_1 e^{-w_1'/RT}$  and  $k_2 e^{-w_2'/RT}$ . If these are unequal an accumulation of electrons on one side of the boundary will occur until the electric forces so set up effect a balance. Let the amounts of work to be done before passage across the boundary from either side be now  $w_1'' + e_1 F$  and  $w_2'' - e_2 F$  where  $w_1'' - w_2'' = w_1 - w_2$  and  $e_1 + e_2 = E$ , the total P.D. between the metals. Then the condition of equilibrium is

$$k_1 \sqrt{T} e^{-\frac{w_1'' + e_1 F}{RT}} = k_2 \sqrt{T} e^{-\frac{w_2'' - e_2 F}{RT}} \quad (10)$$

Let 
$$\frac{w_1 - w_2}{F} = U_0 \quad \text{and} \quad \frac{k_1}{k_2} = K.$$

Then 
$$E = -U_0 + RT/F \log_e K. \quad (11)$$

Hence by comparison with (9)  $E = E_1 - E_2$ .

Now the heat absorbed in passing the junction is equal to

the total energy change  $U$  plus the work done in going up the potential difference  $E^*$ . Our expression for the Peltier coefficient  $q$  is therefore

$$q = E + U = \frac{RT}{F} \log_e K + \xi_2 - \xi_1. \quad (12)$$

Differentiating (11) and (12) we obtain

$$\frac{dE}{dT} = \frac{R}{F} \log_e K = \frac{\gamma_0}{T}$$

$$\frac{dq}{dT} = \frac{dE}{dT} + (\sigma_2 - \sigma_1),$$

since by Kirchhoff's equation the temperature coefficient of the total energy change at the junction must be equal to the difference between the specific heats of electrons in the two metals, i. e.,  $\frac{dU}{dT} = \sigma_2 - \sigma_1$ .

From (5) therefore

$$\frac{dq}{dT} = \frac{dE}{dT} = q_0/T, \quad \dots \dots \dots (13)$$

and to the first approximation,

$$\frac{d^2 q}{dT^2} = \frac{\rho_2 - \rho_1}{T}. \quad \dots \dots \dots (14)$$

Now whereas the conception of the origin of the Peltier effect and the general form of its relation with the corresponding contact P.D.'s which has been developed is entirely in accordance and is a logical development of the whole body of the thermionic theory, quantitatively it depends on the validity of the fundamental thermionic equation. In particular the use of the equipartition value  $RT$  in the denominator of the exponent is open to criticism, and it is assumed without justification that  $k$  is independent of the temperature. It is quite possible, for example, that  $k$  is a function of the specific heat of electrons in the metal, in which case some modification of the thermoelectric equations would be required.

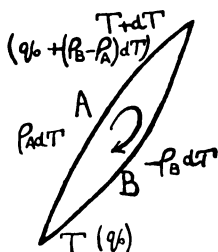
Under these limitations an interesting conclusion can be drawn from (13), which implies that the difference in the contact P.D.'s in thermoelectric circuit accounts for the whole of the e.m.f., i.e., that the Thomson effect in the closed circuit does not contribute to the e.m.f.

This conclusion, which at first sight appears somewhat

\*  $U = U_0 + \xi_2 - \xi_1$  where  $\xi_2$  and  $\xi_1$  are the thermal energies of electrons in the two metals.  $q_0 = A + U_0$ .

† This equation has recently been directly verified by Latimer. Journ. Amer. Chem. Soc. vol. xlv. p. 2136 (1922).

improbable, is made more understandable by the following considerations. In the passage of electrons round a closed circuit of two metals with junctions at different temperatures, the heat effect  $\int(\rho_A - \rho_B)dT$  in the homogeneous conductors due to the heat capacity of electrons is balanced by differences in their thermal energy changes in crossing the two junctions. This is evident from the diagram. The resultant heat effect



is simply  $dE = R \log_e K \cdot dt$ . Hence (13) in no way violates the conservation of energy.

It by no means follows that there is no difference of potential along a homogeneous conductor in which there exists a temperature gradient, only that the P.D. must be the same in all conductors for the same temperature difference.

It must be observed that the equation  $de/dT = q_0/T$  is similar but not identical with the thermodynamical equation (5 A). The difference may be due to the uncertainties in the thermionic equations referred to, but it must also be remembered that in the thermoelectric circuit the reversible effects are necessarily accompanied by certain irreversible phenomena, and as Richardson has recently pointed out\*, "the assumption that the laws of thermodynamics as they apply to reversible cycles can be applied to reversible effects superposed on such a system is one which has never been proved to be necessarily valid."

#### *Summary.*

The statistical theory of metal boundary potentials is developed and an equation giving the relation between the thermionic work functions of metals and the corresponding contact P.D.'s is obtained. The Peltier heat effect at the junction of two metals is accounted for and the various equations of the thermoelectric effect in a circuit of two metals with junctions at different temperatures are completely co-ordinated. On certain assumptions these equations lead to the conclusion that the Thomson P.D. is the same for the same difference of temperature in all conductors.

\* Proc. Roy. Soc. [A], vol. cv, p. 387 (1924).

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LXXVI. *On the Impact of a Solid Sphere with a Fluid Surface and the Influence of Surface Tension, Surface Layers, and Viscosity on the Phenomenon.* By G. ERIC BELL, B.Sc., *Physics Research Laboratory, University College, Nottingham* \*.

[Plate XV.]

THE phenomena attending impact with fluid surfaces were first studied by Worthington†, who traced by means of instantaneous photography the course of events after the impact. He showed that splashes fall into two fairly clearly defined classes, one in which no air is drawn into the liquid, which he calls a “smooth” or “airless” splash, and the other in which a large air-cavity is produced, which he calls a “rough” or “basket” splash. If the falling body be a sphere, quite clean and free from grease, the splash is smooth for low impact-velocities but becomes rough if the velocity is increased, the transition from one to the other being quite sudden. Traces of grease and dust make this “critical velocity” much less, and it is also less if an oil is used instead of water. Worthington attempts an explanation of the effect of dust, and also of the different effect in the case of oil, and shows that any factor which renders the surface shearable produces a rough splash.

\* Communicated by Prof. E. H. Barton, F.R.S.

† Worthington, *Phil. Trans. Roy. Soc.*, A 193. (1897) and A 225. (1900).



Mallock \* develops a simple mathematical theory of the shape of the cavity produced, confining his attention to the case of the impact of a solid sphere with a fluid surface. This theory gives the general shape of the cavity, but does not agree exactly with experiment, and there appear to be contributing factors of which he does not take account.

The object of the present research is to examine the phenomena in more detail, with special reference to the effect of surface-layers on the impinging ball, and the surface tension and viscosity of the liquid, and to try to extend Mallock's theory.

### *Experimental Procedure.*

The general method of experiment is similar to that of Worthington and Mallock, but differs slightly from either. The apparatus is shown diagrammatically in fig. 1. The Leyden-jar battery L has its inner coating connected to one pole of a Wimshurst machine, its outer coating, together with the other pole of the machine, being earthed. The inner coating is then connected to two spark-gaps A and B in series, and finally to earth. The Wimshurst machine is run at a steady rate by means of a small electric motor, and serves to charge up the jars. M and M' are two small electromagnets connected through a key K to a battery of cells. On depressing the key K, the electromagnets release respectively a large ball which falls between the electrodes of the first spark-gap A, and a small ball which falls into the liquid in the tank T.

When the large ball falls through the spark-gap A the resistance of the whole circuit is reduced and the potential-difference established serves to cause a spark to leap across the second gap B. By suitably arranging the height through which the large ball falls, the splash caused by the other one may be photographed at any time.

The balls employed are Hoffmann steel balls, of diameters 1 inch and  $5/16$  inch. The secondary spark-gap B has magnesium electrodes, and produces a very brilliant, highly actinic spark, casting a shadow of the splash which is recorded on the photographic plate P.

As steel balls are used, it is possible to suspend them from the poles of the magnets directly, thus simplifying the arrangements and also avoiding any constraints such as would cause the balls to rotate.

\* Mallock, Proc. Roy. Soc. xev. (1918).

Imperial "Special Rapid" plates (H & D 250) were used, developed with Tabloid "Rytol" or a special developer recommended by the makers of the plates.

The timing caused a certain amount of trouble at first, but by reducing the strength of the magnets by means of the rheostats R and R' so that they only just supported the balls,

Fig. 1.

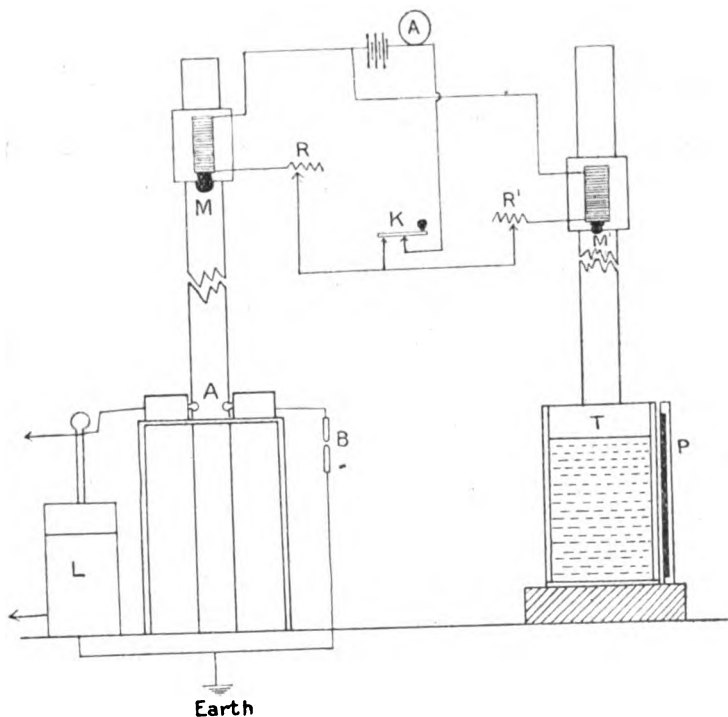


Diagram of Apparatus.

and keeping the electrodes, especially those of the large gap A, clean and polished, this difficulty was overcome and photographs taken under similar conditions "reproduced" with accuracy.

By this means a large number of photographs have been obtained, showing the effect of coating the ball with surface-layers of different substances, of using different liquids, and of changing the viscosity of the liquid.

*Mallock's Theory and Comparison with  
Experimental Results.*

Consider a sphere of density  $\rho$  falling normally with velocity  $v$  into a fluid of unit density. As long as the cavity remains open to the surface the sphere is influenced by (1) a hydrodynamic resistance,  $Av^2$ , proportional to the square of the velocity, (2) a hydrostatic pressure proportional to the depth,  $Bx$ , and (3) an acceleration  $C$ , upwards or downwards according as to whether  $\rho$  is greater than or less than unity.

If we take the axis of  $x$  vertical, the equation to motion for this small time is

$$\dot{v} = -Av^2 - Bx + C. \quad (1)$$

The constants may be eliminated. So long as the cavity remains open, the shot is in the same condition as if mounted at the end of a weightless tube of its own diameter. It is, therefore, subject to a retardation  $g(x'/h)$ , where  $h$  is the depth at which the tube, as weighted by the shot, would float, and  $x'$  the distance from a new origin at  $h$ , and also a retardation  $g(v_1^2/v_0^2)$ , where  $v_1$  is the velocity at  $x'$  and  $v_0$  the "terminal velocity."

We thus have

$$\dot{v} = -g\left(\frac{x'}{h} - \frac{v_1^2}{v_0^2}\right). \quad (2)$$

From this equation, Mallock deduces the space-time curve step by step. However, we may integrate once and obtain the velocity at any time, and also, for special cases, perform the complete integration and obtain a very approximate relation between depth and time.

The equation may be written

$$v_1 \frac{dv_1}{dx'} = -g\left(\frac{x'}{h} - \frac{v_1^2}{v_0^2}\right).$$

Integrating, we have

$$v_1^2 = v_0^2 e^{-\frac{2g}{v_0^2} x'} - \frac{v_0^2}{h} \left(x' - \frac{1}{2} \frac{v_0^2}{g}\right).$$

Inserting the initial conditions, that the sphere is at the surface when  $t=0$ , with a velocity  $v$ , i. e., at  $t=0$ ,  $x' = -h$ , and  $v = v$ , we have

$$v^2 = v_0^2 e^{-\frac{2g}{v_0^2} (h+x')} \left\{ v^2 - \frac{v_0^2}{h} \left(h + \frac{v_0^2}{2g}\right) \right\} - \frac{v_0^2}{h} \left(x' - \frac{v_0^2}{2g}\right). \quad (3)$$

For water, and liquids of similar viscosity (of the order .01) the "terminal velocity"  $v_0$  is very high (for a steel

sphere 5/16 in. diameter  $v_0$  is of the order 2000 cm. per sec.) and the equation of motion (2) may be simplified to

$$v_1 \frac{dv_1}{dx} = -\frac{g}{h} x', \quad . . . . . (4)$$

giving on integration

$$x' = A \sin \sqrt{\frac{g}{h}} t - B \cos \sqrt{\frac{g}{h}} t,$$

or

$$x' = A \sin pt - B \cos pt \quad \text{where } p^2 = g/h,$$

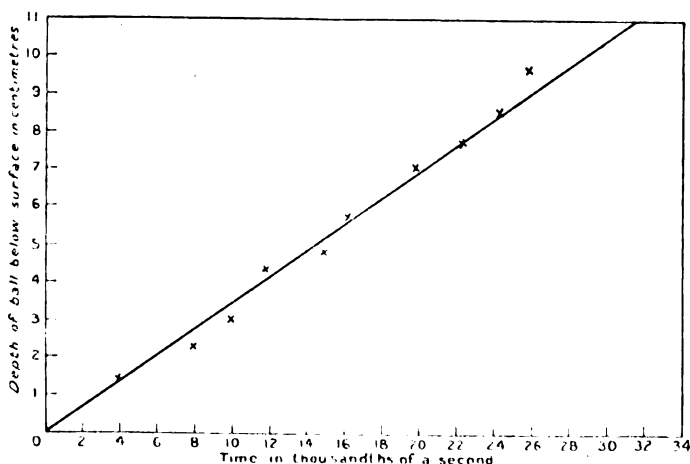
and

$$v_1 = \frac{g}{h} \{ A \cos pt + B \sin pt \}.$$

Inserting the initial conditions that at  $t=0$ ,  $x' = -h$  and  $v_1 = v_0$ , we have

$$x' = v_0 \frac{h}{g} \sin pt - h \cos pt. \quad . . . . . (5)$$

Fig. 2.



Space-time Graph for Sphere in Water.

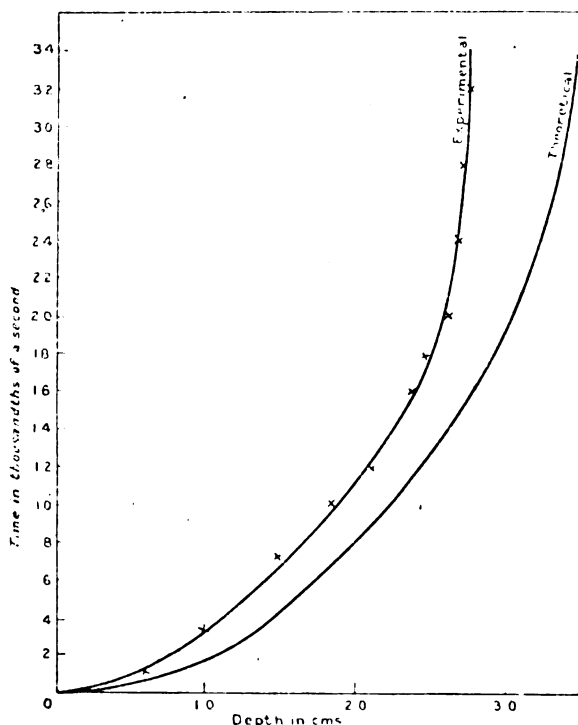
Thus, for the very limited time for which the assumed conditions are valid, the space-time curve is a straight line. That this is substantially true is evident from fig. 2, which gives the experimentally determined space-time curve for a steel sphere dropping into water.

Unfortunately, the equation of motion (2) cannot be integrated completely in its general form, and for viscous liquids

such as glycerine ( $v_0$  for pure glycerine at a temperature of  $17^\circ\text{C}$ . is of the order 23 cm./sec. for a steel ball 5/16 in. diameter) indirect methods must be used in order to obtain the space-time curves.

Fig. 3 shows the curves for glycerine, density 1.26 and viscosity 10. The velocity space-curve has been deduced from equation (3) for an initial velocity of 300 cm. per sec., and the space-time curve deduced from it.

Fig. 3.



Space-time Graph for Sphere in Glycerine.

The curve marked "experimental" has been deduced from the measurement of a large number of photographic records, after correction for the refraction of the light on passing through the tank. The agreement between the two is as good as can be expected. The ball appears to fall more slowly than demanded by the theory, probably because the impact introduces conditions near the surface which have not been considered.

*Shape of the Cavity.*

Mallock also deduces an expression for the shape of the cavity at any time. He assumes that, after the impact, two forces are operative on the liquid, one giving it an outward flow, whose radial component is some function of the velocity  $v_1$ , and the other a hydrostatic pressure, giving the surface a velocity inwards.

If  $\eta$  and  $\xi$  are the coordinates of a point on the surface of the cavity at any time  $t$ ,  $\eta$  being the distance of the point from the surface of a cylinder traced by the circumference of the shot and  $\xi$  its depth, we have

$$\eta = \int_{t_{\xi}}^{t'} [f(v_1) - \sqrt{2g\xi}] dt, \quad \dots \quad (6)$$

the integration limits being the time at which the shot passed the point, and the time under consideration.

Mallock remarks that many forms of  $f(v_1)$  may be found which fit the curve fairly well, but as none have a theoretical basis he takes  $f(v_1)$  as some constant of  $v_1$ , say  $\theta v_1$ , obtaining the result

$$\eta = (t_x - t_{\xi})(\theta v - \sqrt{2g\xi}). \quad \dots \quad (7)$$

Fig. 4 shows the curves deduced from this equation, giving the theoretical shape of the cavity at the time given,  $t=0$  being the time at which the ball is just below the surface.

These figures may be compared with those of Pl. XV, which gives reproductions of the actual photographs, allowance being made for the magnification and distortion due to the refraction of light passing through the tank.

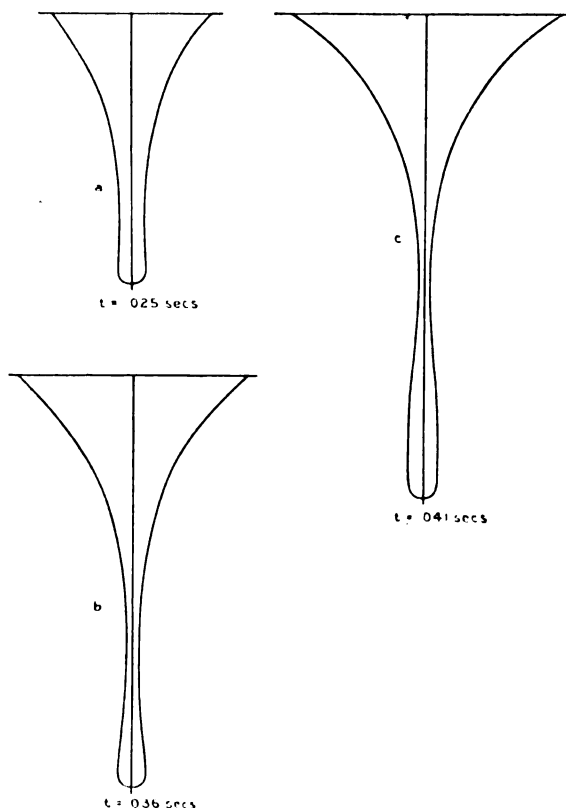
*Influence of Surface Tension*

Equation (7) shows that the shape of the cavity does depend to some extent on the nature of the liquid, in particular on its viscosity, since the time of the descent ( $t_x$  &  $t_{\xi}$ ) and also  $\theta v$  the velocity of radial outflow depend on the viscosity, but no account is taken of the influence of surface-tension.

A detailed comparison of photographs of splashes taken under different conditions seems to show that surface-tension does play a rather important part. The cavity formed when the ball is dropped into turpentine, although of the same general shape as when dropped into water, is slightly wider.

The viscosities of the two liquids are nearly the same, but the surface-tension of turpentine is only 27.3 dynes per cm. against the 72.4 dynes per cm. of water. The same thing is apparent in the case of the ball falling into paraffin oil, although the photographic record is too weak to reproduce.

Fig. 4.



Shape of Cavity deduced from Mallock's Theory.

The shape of the air-cavity at the times given deduced from Mallock's theory for a steel ball  $\frac{1}{16}$  inch diameter falling into water with a velocity under the surface of 300 cm. per sec.

It will further be seen that the cavity is wider when the ball is coated with a thin oil-layer. The mouth of the cavity formed when the ball is coated with paraffin oil and turpentine is much wider than when coated with (solid) paraffin-wax.

This is probably due to the fact that in the first case the cavity is lined with a thin layer of a substance of lower surface-tension. Worthington (*loc. cit.*) noted that when a liquid drop is allowed to fall into a liquid, the cavity is lined with the liquid of the drop itself, thus providing an *a priori* justification for this explanation.

It thus appears that, in addition to the two forces of which Mallock takes account, there is a third one due to surface-tension. This causes a pressure over the walls of the cavity of magnitude  $2T\left(\frac{1}{R} + \frac{1}{r}\right)$ , where  $r$  and  $R$  are the radii of curvature, the direction of the pressure being such as to tend to cause the cavity to collapse. Thus, paraffin oil and turpentine having low surface-tensions, this force tending to close the cavity will be less, and the cavity at any time wider, than in the case of a liquid of higher surface-tension.

#### *Influence of Surface Layers.*

It will be seen from the photographs that surface-layers on the ball have a very pronounced effect on the surface-disturbance, in addition to their effect on the shape of the cavity.

Referring to Pl. XV., figs. 1 (*a, b, & c*) are shadowgraphs of the splash occurring when the ball is wet with paraffin oil, and falls into water. In figs. 2 (*a, b, & c*) the ball has been coated with a thin layer of paraffin-wax, in figs. 3 (*a, b, & c*) it has been wet with water, and in figs. 4 (*a, b, & c*) with turpentine.

Figs. 5 (*a, b, & c*), 6 (*a, b, & c*) and 7 (*a, b, & c*) show the result of the impact of a sphere wet with turpentine, paraffin oil, and water respectively falling into turpentine.

In the cases shown in figs. 8 (*a, b, & c*) a layer of paraffin oil 1.4 cm. thick has been floated on the surface of the water, and the ball wet with paraffin oil.

In all these cases the velocity of the ball just below the surface was 300 cm. per sec., and the resulting splash "rough" in each case. With this velocity a perfectly smooth, clean, and well-polished ball invariably gave a smooth splash.

When the ball is wet with water and falls into either water or turpentine, the cavity closes over very quickly, as is shown in figs. 3 & 7. The figures in this case do not reproduce so accurately as in the other cases, owing to the fact that it is extremely difficult to get a film of water to adhere evenly.

The general shape of the cavity does not vary much, except



for such slight differences as are accounted for by varying surface-tensions.

When the ball is wet with paraffin oil and falls into turpentine, the result is very curious, the cavity collapsing very quickly at the top, in much the same way as when the ball is wet with water and falls into either water or turpentine.

Finally, in one series of experiments a layer of paraffin oil 1.4 cm. thick was floated on the surface of the water and the ball wet with paraffin oil. The object of this was to observe the effect at the interface of two liquids. As will be seen from the photographs, the ball appears to penetrate into the second liquid without dragging the first liquid after it.

The difference in the surface disturbance under varying conditions is more noticeable.

The ball wet with paraffin oil gives very similar surface effects to the ball coated with paraffin wax, both being quite different from the case in which the surface of the ball is wet with turpentine. When the ball is wet with turpentine and falls into turpentine, the surface-disturbance is very similar to that when the ball wet with turpentine falls into water, and also to the case of a ball wet with paraffin oil falling into paraffin oil.

A slight, though remarkable difference exists, however, between the surface-disturbances shown in figs. 5 & 8 and the other cases, for it appears that when the ball is coated with the same liquid as that upon which it impinges, the upshot rim tends to close in more rapidly at the top.

#### *Influence of Viscosity.*

Figs. 9-11 show the effect of the impact of a clean and well-polished steel ball 5/16 in. diameter with the surface of a glycerine-water mixture of different viscosities.

In the first series, figs. 9 (*a, b, & c*) the viscosity of the glycerine and water mixture was 4.5 and the shape of the cavity appears to be very little different from the previous examples. The neck tends to form earlier and of course the ball falls more slowly. A glycerine and water mixture of viscosity 9 gives the effects shown in figs. 10 (*a, b, & c*). Again we have a very similar effect, although the surface conditions are quite different from those produced when liquids of low viscosity are used.

With increasing viscosity, however, the characteristics of

the cavity alter fundamentally, and with viscosity 12 we obtain the effect shown in figs. 11 (*a, b, & c*). It will be noticed that the cavity is always much narrower, and that the liquid appears to cling to the upper surface of the ball. The very pronounced neck has almost disappeared, although there is still a minimum diameter. Instead of opening out quickly below the neck as previously occurred, we see that the lower part of the cavity is nearly cylindrical, and that it retains this form for a comparatively long time. When finally the cavity collapses, it does so from the bottom, gradually, not suddenly collapsing from the neck as is the case for low viscosities.

Mallock's theory fits the experimental curves fairly well up to viscosity 9, but the author has been unable to deduce from theory the shape shown in figs. 11. It seems probable that the expression for radial outflow  $\theta v$  is not applicable,—possibly some more complicated function of  $v$  could be found which would make equation (7) apply. In general terms the theory appears valid, for the numerical value of  $f(r)$  of equation (6) will almost certainly decrease with increase of viscosity, thus making  $\eta$  smaller, and also making it become negative sooner.

#### *The Striæ on the Figures.*

On all the photographs obtained using liquids of very low viscosity there appear nearly horizontal striæ, as is clearly seen in the figures of Plate XV.

Examination of the photographs shows that

- (1) The striæ are always nearly horizontal.
- (2) They never appear in the liquid below the air-cavity.
- (3) They extend on either side of the cavity for some distance.

The origin of these is not at all clear, but it is possible that they may be due to some kind of waves—probably compressional. Such waves would produce places of alternate compression and rarefaction, accompanied by corresponding changes in refractive index. Regular variations of refractive index would have a focussing effect, and thus account for the comparatively clear definition and brilliance of the bright lines.

The explanation is only tentative. At first it was thought that the striæ were due to reflexion from the plate-holder and elsewhere; all parts of the apparatus were then painted

dead-black and a new plate-holder constructed having a face of the dead-black matt paper in which plates are usually wrapped, but this did not eliminate the markings. Further, the fact that the depth to which the striæ extend in the liquid is related to the depth of the air-cavity tends to show that the markings are due to some disturbance in the liquid and not to fortuitous circumstances.

Other possible explanations have been considered and abandoned. It is known that if a large bubble be allowed to ascend in the liquid contained in a fairly wide tube, it assumes a more or less cylindrical form with hemispherical ends, and that the "walls" of the bubble are covered with beautiful small ripples. However, since the markings appear in the liquid outside the cavity, this explanation of the striæ observed does not seem to hold.

#### *Summary.*

In this paper the phenomena attending the impact of a solid sphere with a fluid surface are studied, with special reference to the effect of (1) the surface-tension of the liquid, (2) surface-layers on the ball, and (3) the viscosity of the liquid. It is shown that the theory given by Mallock holds fairly well for liquids of low viscosity, but evidence is given that surface-tension should be introduced into the theory. Surface-layers affect both the shape of the air-cavity and also (in a more pronounced manner) the surface-disturbance. The effect on the shape of the cavity is such as is accounted for by varying surface-tension, but no explanation can be given for the varying surface-conditions. When liquids of high viscosity are used the shape of the cavity changes fundamentally, and Mallock's theory in its simplified form does not appear to be applicable. Finally the nature and origin of certain striæ which appear on the photographs is discussed, and a tentative explanation given.

In conclusion the author desires to thank Prof. E. H. Barton, D.Sc., F.R.S., for his kindly interest, aid, and criticism, the Department of Scientific and Industrial Research for a grant by the aid of which the research has been carried out, and the Imperial Plate Company, Cricklewood, for technical advice on the manipulation of their plates under these difficult conditions.









LXXVII. *The Determination of Molecular Diameters from Surface-Tension Measurements.* By SERGIUS MOKROUSHIN \*.

THE methods for determination of molecular dimensions may be divided into (1) kinetic or dynamic, and (2) statistical methods. Values of molecular diameter from the kinetic theory of gases depend upon the kinetic energy of the molecules (Jäger, *Handbuch der Physik*, Winkelmann, 'Wärme,' p. 761, 1906), and especially upon the distances of approach one to another at the time of collision. The greater the momentum of a molecule the nearer will it approach another during the period of collision. For this reason the molecular diameters as determined by Lenard from ionization measurements are less than those found from measurements of viscosities of gases (Timiriaseff, 'Kinetic Theory of Matter,' p. 161, 1923). Lenard (*Ueber Kathodenstrahlen*, Nobel Vorlesung, 1906) found that when molecules are subjected to bombardment by electrons, the diameters so calculated continually decrease as the electron velocity is increased and become ultimately of the order of  $10^{-12}$  cm., i. e. one ten-thousandth of the average value found from viscosity measurements.

The surface-tension method allows us to determine a value of the molecular diameter in a liquid or gas, and makes it independent of the determination of mean free path resulting from collisions. Naturally this method must be referred to statistical methods and to those involving the use of van der Waals's equation of state (Lewis, 'A System of Physical Chemistry,' Kinetic Theory, p. 13), in which  $6/7$  of the term  $b$  appears to be the volume actually occupied by the molecules themselves, and whence, knowing the Avogadro number, we may easily determine the molecular diameter.

Statistical methods depend upon the determination of molecular forces of attraction observable when the distances between molecules become less than  $10^{-7}$  cm. (Langmuir, Lewis, *l. c.* p. 762). Consequently we may consider this value as the order of magnitude of the largest radius of the sphere of attraction of one molecule for another, or, as the diameter of the molecule.

We may regard the surface of a liquid as a unimolecular layer, since it has been shown by Lord Rayleigh ('Nature,' xlii. p. 43, 1890) that the thickness of an oil film spread on

\* Communicated by Prof. F. G. Donnan, F.R.S.



water is of the order of  $1.6 \times 10^{-7}$  cm., and by Devaux (Journ. Phys. iii. (4) p. 450, 1904) that films of paraffin and metal sulphides give thicknesses of the same order. This has been more definitely shown by Langmuir (Journ. Amer. Chem. Soc. xxxix. p. 1848, 1917). Hence we may assume that the surface-tension is equal to the force of attraction of one molecule for another. On the other hand, we know that the latent heat of vaporization has to be used in overcoming the forces of cohesion (the "disgregation" of Clausius), and for the performance of external work by the gas (Graetz, *Handbuch der Physik*, Winkelmann, 'Wärme,' p. 1087).

The internal heat of vaporization is given by the equation

$$Q = \lambda_i + p(r_1 - v), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $\lambda_i$  = internal latent heat of vaporization,  
 $p$  = pressure of vapour,  
 $v$  = volume of liquid,  
 $r_1$  = volume of vapour formed.

Since  $v$  is small compared with  $r_1$  when the temperature is far from the critical point, we may express equation (1) as

$$Q = \lambda_i + p r_1. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Then if  $r_1$  is the volume per gram molecule, we have by the Clapeyron equation

$$Q = \lambda_i + RT, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $R$  is the universal gas constant = 1.985 cal., and  $T$  = absolute temperature of vaporization.

Then if we assume that the internal latent heat of vaporization is used in increasing the surface-energy in the process of change of state, i. e. increasing the free surface of the molecules, we have

$$Q = \sigma(S - S_0) + RT, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where  $\sigma$  = surface-tension,  
 $S$  = surface of molecules of vapour,  
 $S_0$  = free surface of vaporization of liquid.

The term  $S_0$  being small compared with  $S$ , we may write

$$Q = \sigma S + RT, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

whence  $\sigma S = Q - RT$ , . . . . . (6)

or expressing in C. G. S. units we have

$$\sigma S = 4.189 \times 10^7 (Q - RT),$$

where  $4.189 \times 10^7$  ergs is the mechanical equivalent of heat. The molecular surface in a vapour,  $S = \pi d^2 N$  where  $N$  is the Avogadro number,  $= 6.85 \times 10^{23}$  (Perrin, Lewis, *l. c.* p. 29). Hence the molecular diameter may be easily determined from the equation

$$d = \sqrt{\frac{4.189 \times 10^7}{\pi N}} \cdot \sqrt{\frac{Q - RT}{\sigma}}, \quad . . . (7)$$

or since  $\sqrt{\frac{4.189 \times 10^7}{\pi N}}$  is a constant  $= 4.41 \times 10^{-9}$ , we may

write  $d = K \sqrt{Q - RT}$  . . . . . (8)

Table I. shows some molecular diameters, calculated by means of this equation, compared with determinations by other methods.

TABLE I.  
Molecular diameters  $\times 10^8$ .

Substance.	Ionization. Lenard.	Viscosity of Gases. Sutherland <sup>1</sup> .	Equation of State. Van der Waals <sup>2</sup> .	Diffusion Coefficient in Aqueous Solution. Svedberg <sup>3</sup> .	Kinetic Theory and Capillary Constant, Jäger <sup>4</sup> .	Equation (8).
N <sub>2</sub> .....	1.00	2.95	6.7	—	—	4.94
H <sub>2</sub> .....	0.63	2.17	4.7	1.6	—	4.48
O <sub>2</sub> .....	—	2.71	6.1	4.6	—	4.6
H <sub>2</sub> O.....	1.02	—	—	—	5.1	5.12
Cl <sub>2</sub> .....	—	3.74	—	5.0	—	5.24
Br <sub>2</sub> .....	—	—	—	7.6	—	5.82

<sup>1</sup> Sutherland, *Phil. Mag.* xix. p. 25 (1910).

<sup>2</sup> Lewis, 'A System of Physical Chemistry,' Kinetic Theory 13.

<sup>3</sup> Svedberg, *Z. phys. Chem.* lxxvii. p. 105 (1909).

<sup>4</sup> Jäger, *Handbuch der Physik*, Winkelmann, 'Wärme,' p. 767.

Jäger (*l. c.*) determined the value of molecular diameter, as we have done, as a function of the surface energy, but he connected this surface energy not with the latent heat of vaporization, but with the kinetic energy of the vapour molecules, assuming that every particle in the change of state divides into at least two particles, and that the surface energy increases in this way and becomes equal to the kinetic energy of the particles or molecules. The diameter for water determined by Jäger,  $5 \cdot 10 \times 10^{-8}$  cm., is the same as that obtained in this paper,  $5 \cdot 12 \times 10^{-8}$  cm.

By application of the Trouton Rule (according to which  $\frac{Q}{T_{\text{boil}}} = \text{constant} \sim 21$ ), we may easily calculate the molecular diameter at the boiling-point. Equation (8) then takes the form  $d = K \sqrt{\frac{19T}{\sigma}}$ , and putting  $K \sqrt{19} = K_1$ , we have

$$d = K_1 \sqrt{\frac{T}{\sigma}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where  $K_1 = 1 \cdot 92 \times 10^{-8}$ .

From equation (4) it follows that the latent heat of vaporization depends upon the value of the free surface of a liquid, and diminishes as the surface increases. Moullerrigne (*Journ. Phys.* v. (3) p. 159, 1896) draws attention to the dependence of latent heat of vaporization upon the form of the surface.

I would like to point out that, owing to difficulties of obtaining reference literature, it is possible that reports of investigations of this type may have appeared and not been seen by me.

In conclusion I wish to express my deepest gratitude to Professors A. V. Thoubnikoff and R. E. Makovetzky for their kind interest and valuable information.

Laboratory of Physical Chemistry,  
University of Oural, Ekaterinburg,  
May 5th, 1923.

LXXVIII. *On the Determination of the Frequencies of the Resonant Tones of some Compound Resonators used in Acoustical Instruments.* By E. T. PARIS, D.Sc., F.Inst.P.\*

§ 1. *Introduction.*

**R**ESONANCE, or "tuning," is employed in nearly all instruments used for measuring the amplitude of sound waves in air. Sensitive Rayleigh disk instruments, for example, are generally made with double resonators, and depend for their sensitiveness largely on the response of a resonator to the particular tone which it is desired to measure †. Other well-known tuned instruments are the phonometer designed by the late Professor A. G. Webster ‡, and the selective hot-wire microphone §. In the phonometer, tuning is performed by means of a single (variable) Helmholtz resonator, while in the hot-wire microphone it is accomplished by a single or double resonator according to the degree of sensitiveness required.

It is clearly important that means should be available for calculating the frequencies of resonators used in such instruments, and, conversely, for determining the dimensions of resonators which are required to respond to given tones. The formula for the natural frequency of a Helmholtz resonator (as used in the phonometer and the singly-resonated hot-wire microphone) is well known and has stood the test of experience. The theory has also been given of some of the more usual forms of double resonator employed in Rayleigh disk instruments and hot-wire microphones ||. There remains, however, a number of other resonators—some double and some of a more complicated kind—which have been found serviceable in the construction of acoustical instruments, but which have so far received little attention from a theoretical point of view. It is the purpose of the present paper to give a brief description of

\* Communicated by Prof. H. W. Porter, D.Sc., F.R.S., F.Inst.P.

† See, for example, the description of the "Microtonometer" by Professor C. V. Boys in 'The Dictionary of Applied Physics,' iii. p. 723; or the instrument figured by F. R. Watson, 'Acoustics of Buildings,' p. 93 (1923).

‡ Details are given in 'Nature,' ex. pp. 42-45 (1922); and Proc. Roy. Inst. xxvii. pp. 406-411 (1924).

§ W. S. Tucker and E. T. Paris, Phil. Trans. A, cexxi. pp. 389-430 (1921).

|| Rayleigh, 'Theory of Sound' (2nd ed.), ii. pp. 189-192, and Phil. Mag. xxxvi. pp. 365-376 (1918); E. T. Paris, Proc. Roy. Soc. A, ci. pp. 391-410 (1922).

these resonators and the ways in which they are employed, and to show how equations can be derived from which their resonance frequencies are calculable by the use of graphical methods. Although the work is mainly theoretical, a few experiments are described which illustrate the application of some of the theoretical formulæ.

## § 2. *Extension of the Theory of the Boys Double Resonator.*

The Boys double resonator is a combination of a Helmholtz resonator with a stopped pipe. The Helmholtz resonator is attached to the pipe as shown diagrammatically in fig. 1 or fig. 2, and the sound-detecting apparatus (Rayleigh disk or hot-wire grid) is placed in the short neck leading from the pipe into the Helmholtz resonator (c, figs. 1 & 2). The

Fig. 1.

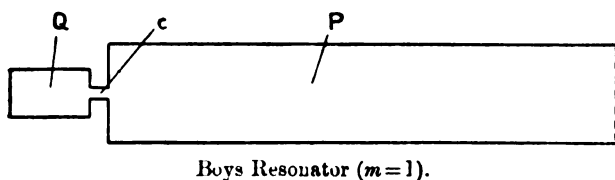
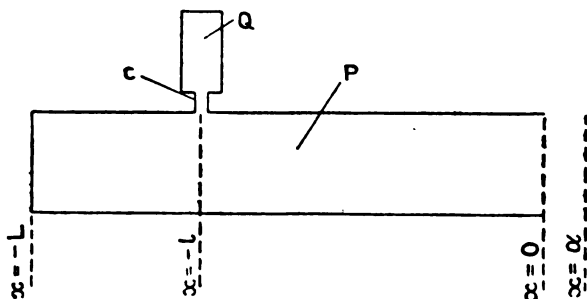


Fig. 2.



advantage of the arrangement is that when the resonator responds to a sound of suitable frequency the air in the neck oscillates with an amplitude which may be hundreds of times greater than the amplitude in the original wave. This type of resonator was first used by Boys in the construction of Rayleigh disk instruments.

The particular variety of Boys double resonator shown in fig. 1, in which the Helmholtz resonator (Q) is attached at

the closed end of the pipe (P), has already received attention in connexion with its application in the construction of doubly-resonated hot-wire microphones. The frequencies of the resonant tones are given by values of  $n$  which satisfy the equation \*

$$\tan \frac{\pi n}{2n_0} = - \frac{2\pi\sigma}{ac} n_1 \left( \frac{n}{n_1} - \frac{n_1}{n} \right), \quad \dots \quad (1)$$

where  $n_0$  is the number of vibrations per second in the fundamental resonant tone of the pipe;  $n_1$  is the number of vibrations per second in the fundamental resonant tone of the Helmholtz resonator†;  $c$  is the hydrodynamical conductance of the neck of the Helmholtz resonator; and  $a$  is the velocity of sound in air. The values of  $n$  obtained in particular cases by a graphical solution of (1) have been found to be in good agreement with observation.

The form of resonator to which it is now desired to direct attention is that shown in fig. 2, which differs from that shown in fig. 1 in that the Helmholtz resonator is attached to the pipe at some distance from the closed end. This kind of resonator is important on account of its usefulness in the construction of extremely sensitive instruments, such as Boys's microtonometer. In connexion with hot-wire microphones, it is employed in cases where instruments are required which are to be very sensitive over a narrow range of frequencies and are to be used with an amplifier and telephones or vibration-galvanometer. (For the "bridge" method of using the hot-wire microphone, the form described in the next section is more suitable.)

In order to obtain an equation from which the frequencies of the resonant tones can be calculated, we proceed as follows. The loss of acoustical energy from the resonator—due to viscous forces and the escape of sound from the mouth of the resonator—is left out of account, and those frequencies are sought which are compatible with a stationary motion of the air contained within the walls of the resonator and a surface of no pressure variation at the mouth.

It is convenient to suppose that the pipe is straight; although the subsequent work would need no serious modification if the pipe were curved, provided that the cross-sectional area remained the same throughout its length. Thus, let the axis of the pipe be parallel to the axis of  $x$ , and

\* Proc. Roy. Soc. A, ci. p. 396 (1922). A slight alteration is made in the notation.

† The overtones of the Helmholtz resonator are left out of account because of their relatively high frequencies.

let the open end lie in the plane  $x=0$ , and the closed end in the plane  $x=-L$ . The dimensions of the orifice of the Helmholtz resonator being small compared with the length of the pipe, the position of the resonator can be defined with sufficient accuracy by saying that the orifice lies in the plane  $x=-l$  (fig. 2). It will be assumed that the motion of the air inside the pipe takes place parallel to the axis of  $x$  except near the orifice of the Helmholtz resonator, say from  $x=-l+\beta$  to  $x=-l-\beta$ . Let  $\phi_1$  be the velocity-potential of the motion from the open end to  $x=-l+\beta$ , and  $\phi_2$  the velocity-potential from  $x=-l-\beta$  to  $x=-L$ . Also let  $\alpha$  be the correction for the open end, and let  $x'=x+\alpha$ ,  $L'=L+\alpha$ ,  $l'=l+\alpha$ , etc., so that  $x'$ ,  $L'$ ,  $l'$ , etc., are reduced lengths of the pipe. In accordance with the assumed stationary nature of the motion, the general expressions for  $\phi_1$  and  $\phi_2$  can be written

$$\left. \begin{aligned} \phi_1 &= (A_1 \sin kx' + B_1 \cos kx') \cos kat, \\ \phi_2 &= (A_2 \sin kx' + B_2 \cos kx') \cos k(at + \theta), \end{aligned} \right\} \quad (2)$$

where  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$ , and  $\theta$  are constants as yet undetermined, and  $k=2\pi/\lambda$ ,  $\lambda$  being the wave-length.

The condition to be satisfied at  $x'=0$  ( $x=\alpha$ ), there being no escape of energy from the pipe, is that there shall be no variation of the pressure, so that

$$(\partial\phi_1/\partial t)_{x'=0} = 0,$$

and hence  $B_1=0$ . At the closed end,  $\phi_2$  must be such that the velocity is zero, that is

$$(\partial\phi_2/\partial x')_{x'=-L'} = 0,$$

so that

$$B_2 = -\cot kL' \cdot A_2.$$

The expressions for  $\phi_1$  and  $\phi_2$  thus become

$$\left. \begin{aligned} \phi_1 &= A_1 \sin kx' \cdot \cos kat, \\ \phi_2 &= -A_2 \operatorname{cosec} kL' \cos k(x' + L') \cdot \cos k(at + \theta). \end{aligned} \right\} \quad (3)$$

It remains to put in the conditions to be satisfied by  $\phi_1$  and  $\phi_2$  in that part of the pipe which is near to the orifice of the Helmholtz resonator (*i. e.* from  $x'=-l'+\beta$  to  $x'=-l'-\beta$ ). In order to do this, use will be made of a method of approximation which is frequently of service in such cases. The method consists in assuming that the irregular motion due to the presence of the Helmholtz resonator is confined to a volume the dimensions of which

are so small compared with the wave-length that the actual motion at any instant is the same as it would be if the fluid occupying this volume were incompressible\*. Let  $\sigma$  be the cross-sectional area of the pipe, and  $dq/dt$  the rate (c.c. per sec.) at which fluid is passing into the Helmholtz resonator. Then one of the conditions to be satisfied by  $\phi_1$  and  $\phi_2$  in the neighbourhood of the orifice of the resonator is (on the above assumption)

$$\sigma \left\{ \left( \frac{\partial \phi_1}{\partial x'} \right)_{x'=-l'+\beta} - \left( \frac{\partial \phi_2}{\partial x'} \right)_{x'=-l'-\beta} \right\} = \frac{dq}{dt} \quad (4)$$

Now  $\beta$  is small compared with the wave-length (at most comparable with the end correction), and therefore, if those cases are excluded in which the Helmholtz resonator is close to the open end of the pipe, the above equation may be simplified by neglecting  $\beta$  in comparison with  $l'$ . The simplified approximate condition is

$$\sigma \left( \frac{\partial \phi_1}{\partial x'} - \frac{\partial \phi_2}{\partial x'} \right)_{x'=-l'} = \frac{dq}{dt} \quad (5) \dagger$$

The other condition which must be fulfilled in the neighbourhood of the Helmholtz resonator is the continuity of the pressure, and is expressed by

$$\partial \phi_1 / \partial t = \partial \phi_2 / \partial t \text{ when } x' = -l'. \quad (6)$$

From this condition we see that  $\theta=0$ ; and since all adjacent potentials of the type (2) with which we shall have occasion to deal must satisfy a condition of the type (6), the arbitrary phase-angle  $\theta$  will be assumed to be zero in all cases.

Let  $\psi$  be the velocity-potential inside the Helmholtz resonator, and  $Q$  the volume of the resonator. Then

$$dq/dt = c(\phi_{-l'} - \psi), \quad \psi = (a^2/Q) \int q dt, \quad (7)$$

where  $\phi_{-l'}$  is the limiting value of  $\phi_1$  or  $\phi_2$  when  $x' \rightarrow -l'$ , and  $c$  is the conductance of the orifice. Also let

$$4\pi^2 n_1^2 = a^2 c / Q,$$

so that  $n_1$  is the number of vibrations per second in the fundamental tone of the resonator, and let  $2\pi n = ka$ .

\* Rayleigh, 'Theory of Sound' (2nd ed.), ii. p. 66.

† A condition of this form is given by Rayleigh to indicate the method to be followed in the case of a pipe with lateral openings (Sci. Papers, i. p. 50).



Then we find from (7) :

$$\frac{dq}{dt} = \frac{c}{1 - (n_1^2/n^2)} \phi_{-t} \dots \dots \dots (8)$$

From (3) and (5) we have

$$A_2 = A_1 \sin kl' \sin kL' \sec k(L' - l'),$$

and substituting the values of  $\phi_1$  and  $\phi_2$  from (3) in (5) and using the value of  $A_2$  just given, we obtain

$$dq/dt = \sigma k A_1 \{ \cos kl' - \sin kl' \tan k(L' - l') \}. \dots (9)$$

Equating this value of  $dq/dt$  to that given in (8), and putting in the value of  $\phi_{-t}$  obtained from (3), we find, as the equation for determining the frequencies of the resonant tones,

$$- \frac{c}{1 - (n_1^2/n^2)} \sin kl' = \sigma k \{ \cos kl' - \sin kl' \tan k(L' - l') \}$$

for

$$\cot kl' - \tan k(L' - l') = - \frac{2\pi\sigma}{ac} n_1 \left( \frac{n}{n_1} - \frac{n_1}{n} \right). \dots (10)$$

Let  $l' = mL'$ . Then, if  $n_0$  is used to denote the fundamental frequency of the pipe, we have

$$L' = a/4n_0, \quad kL' = \pi n/2n_0, \quad \text{and} \quad kl' = m\pi n/2n_0,$$

and equation (10) may be rewritten in the following form, which is more convenient for the purpose of calculation :

$$\cot (m\pi n/2n_0) - \tan \{ (1-m)\pi n/2n_0 \} = - \frac{2\pi\sigma}{ac} n_1 \left( \frac{n}{n_1} - \frac{n_1}{n} \right). \dots (11)$$

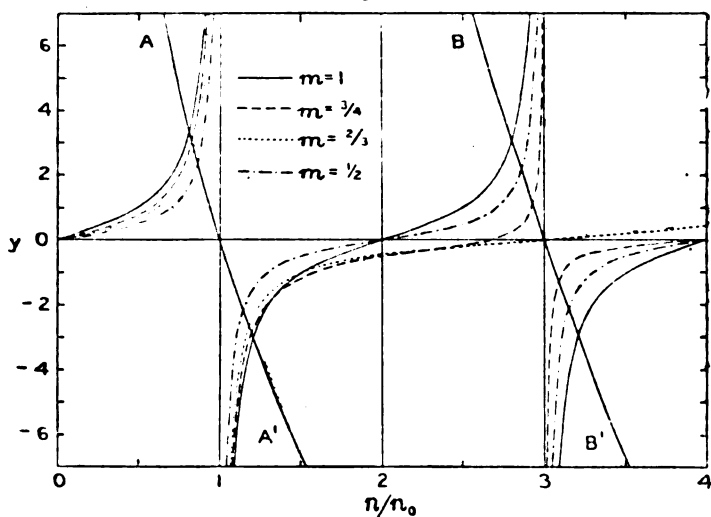
In order to find the resonant tones graphically, write  $Y_1$  for the left-hand side of (11) and  $Y_2$  for the right-hand side, and plot values of  $Y_1$  and  $Y_2$  as ordinates against values of  $n/n_0$  as abscissæ. The curves  $y = Y_1$  and  $y = Y_2$  will intersect with one another at a number of points, and the abscissæ of these points give the values of  $n/n_0$  at which the resonant tones occur. To find the effect of changing  $l'$  (or  $mL'$ ), *i. e.* the distance of the resonator from the open end of the pipe, the  $Y_1$  curves may be plotted for a number of selected values of the parameter  $m$ . The curves  $y = Y_1$  when  $m = 1$ ,  $m = \frac{2}{3}$ ,  $m = \frac{2}{3}$ , and  $m = \frac{1}{2}$ , and  $n/n_0$  is between 0 and 4, are shown in fig. 3.

When  $m$  is unity,  $Y_1$  is simply the tangent of  $\pi n/2n_0$ . The position of the resonant tones and the way in which they

are affected by the tuning of the Helmholtz resonator have already been discussed\*.

As an example of the shift in the position of the resonant tones caused by varying  $m$ , let  $n_1 = n_0$  (that is, let the Helmholtz resonator be tuned to the fundamental of the pipe) and let  $2\pi\sigma n_1/ac = 8$ . The curve  $y = Y_2$  is shown at  $AA^1$  in fig. 3. The intersections with the  $Y_1$  curves indicate that for each value of  $m$  there is one resonant tone below  $n_0$  (between  $0.8 n_0$  and  $0.9 n_0$ ) and another tone above  $n_0$  (between  $1.1 n_0$  and  $1.3 n_0$ ). We see also that for this value of  $2\pi\sigma n_1/ac$

Fig. 3.



Graphical Solution of Equation (11).

decrease in the value of  $m$  causes each of these tones to move inwards towards  $n_0$ . By choosing a smaller value for  $2\pi\sigma n_1/ac$ , however, the slope of the curve  $AA^1$  can be diminished in the region under consideration, and by this means the interval from the tone next above  $n_0$  to the one below it can be increased. If  $2\pi\sigma n_1/ac$  is so small that the intersections indicating the frequencies of the upper tone lie between  $n = 1.5 n_0$  and  $n = 2 n_0$ , then a decrease in  $m$  no longer produces a decrease in the frequency of the upper tone in every case. It can easily be seen from the figure that if  $N$  is the frequency of the upper tone when  $m = 1$ , then the frequency is raised if  $m$  is decreased to  $\frac{3}{4}$ , is lowered

\* Proc. Roy. Soc. A, ci. pp. 400, 401 (1922).

slightly when  $m$  is further decreased to  $\frac{2}{3}$  (but still remains above  $N$ ), and falls below  $N$  when  $m = \frac{1}{2}$ .

In addition to the lowest pair of tones, there is a series of tones whose frequencies are not far removed from those of the overtones natural to the pipe. These are also given by the intersections of the  $Y_2$  curve, of which  $AA^1$  (fig. 3) is a portion, with the  $Y_1$  curve. When  $n$  is great,  $Y_2$  approaches the value  $-(2\pi\sigma/ac)n$  asymptotically, and it is evident that the intersections take place to the right of the asymptotes to the  $Y_1$  curve at  $n/n_0=3$ ,  $n/n_0=5$ ,  $n/n_0=7$ , etc., so that the overtones of the compound resonator are all higher than those natural to the pipe.

The form of the  $Y_1$  curve when  $m = \frac{2}{3}$  is exceptional and demands special attention. Unlike the other curves, it does not pass from  $+\infty$  to  $-\infty$  as  $n/n_0$  passes through the value 3, and consequently one mode of vibration in the neighbourhood of  $3n_0$  appears to be lost. The reason for this is that when  $m = \frac{2}{3}$  the orifice of the Helmholtz resonator is situated at a loop of the first overtone of the pipe, and its presence in this position has no effect on the motion within the pipe when  $n = 3n_0$ . In the theoretical treatment it has been assumed that the motion in the orifice (measured by  $dq/dt$ ) does not vanish for any of the resonant modes of vibration of the combination, whereas modes are actually possible in which  $dq/dt = 0$ , namely those which occur when the orifice is situated at a loop of one of the overtones characteristic of the pipe. In order to complete the solution when  $m = \frac{2}{3}$ , we must regard the vertical lines  $n/n_0=3$ ,  $n/n_0=9$ ,  $n/n_0=15$ , etc., as portions of the  $Y_1$  curve, remembering that  $dq/dt = 0$  for all modes whose frequencies are given by intersections with these lines.

A similar state of affairs occurs whenever the orifice is at a loop of one of the overtones of the pipe, *i. e.* whenever  $m$  has a value  $r/s$  such that  $r$  is an even integer and  $s$  is an odd integer greater than  $r$ .

These results are illustrated in fig. 3, where  $BB'$  is a portion of the  $Y_2$  curve drawn for the particular case when  $n_1 = 3n_0$ , that is when the Helmholtz resonator is tuned to the first overtone of the pipe. The value of  $2\pi\sigma n_1/ac$  is taken to be 22, and fig. 3 shows that the tones on each side of  $3n_0$  are most widely separated when  $m = 1$ . When  $m = \frac{2}{3}$  the interval from the upper to the lower tone is considerably diminished, and as  $m$  approaches the value  $\frac{1}{2}$  the interval approaches unity until when  $m = \frac{1}{2}$  there is but one tone, *viz.*  $n = 3n_0$ . In this case, however,  $dq/dt = 0$  as explained above. After  $m$  has passed through the value  $\frac{1}{2}$  the two

tones move apart, and when  $m=\frac{1}{2}$  they are again well separated.

The above remarks indicate the general nature of the effects to be observed when the Helmholtz resonator is tuned to the fundamental or to the first overtone of the pipe. The position of the resonant tones can be found in a similar manner for any tuning of the component resonators, but there are some special cases which call for attention.

These special cases are all associated with the occurrence of a loop at  $x' = -l'$ , and in order to investigate them, it will be convenient to regard the compound resonator under consideration as a *triple* resonator consisting of the following components:—

- (i) An open pipe extending from  $x' = 0$  to  $x' = -l'$ ;
- (ii) A stopped pipe extending from  $x' = -l'$  to  $x' = -L'$ ;
- and (iii) The Helmholtz resonator.

We first note that all the  $Y_1$  curves cross the axis  $y=0$  at certain places, and that if the Helmholtz resonator is tuned to the value of  $n$  where the crossing occurs, its frequency appears unaltered as one of the resonance frequencies of the combination. For example, if  $n_1 = 2n_0$ , the frequency  $2n_0$  appears as one of the resonance frequencies of the combination when  $m=1$  or when  $m=\frac{1}{2}$ .

In these cases the intersections between the  $Y_1$  and  $Y_2$  curves lie on the axis  $y=0$ ; that is to say, the tuning of the Helmholtz resonator is such that its frequency  $n_1$  is a root of  $Y_1=0$  treated as an equation in  $n$ . It can be shown from equation (11) that the roots of  $Y_1=0$  are those values of  $n$  which would produce in the open-pipe component (i), or in the stopped-pipe component (ii), or possibly in both, a vibration which would have a loop at  $x' = -l'$ . These values of  $n$  are therefore the resonance frequencies of the components (i) and (ii). There are two cases to be considered:—

(a) Let  $n'$  be the frequency of the fundamental (or one of the overtones) of the component (i). Then this will be one of the resonance frequencies of the compound resonator if either the Helmholtz resonator or the component (ii) is also tuned to  $n'$ . In the former case there will be no vibration whatever in that part of the pipe which lies between the Helmholtz resonator and the stopped end at  $x' = -L'$ , this being one of those cases in which sound is sometimes said to be “absorbed” by a resonator\*, so that the component (ii)

\* Cf. Rayleigh, ‘Theory of Sound’ (2nd ed.), ii. p. 210.

is idle\*. In the latter case the orifice of the Helmholtz resonator is at a loop of one of the overtones of the stopped pipe  $1'$ , and hence (as described above) the component (iii) is idle, that is  $dq/dt=0$ .

(b) Let  $n''$  be the frequency of the fundamental (or one of the overtones) of the component (ii). Then this will be one of the resonance frequencies of the compound resonator if either the Helmholtz resonator or the component (i) is also tuned to  $n''$ . In the former case, theory indicates that there should be no vibration at all in the component (i). In practice this is evidently impossible, but it suggests that in special cases a small vibration of the right frequency in (i) may be sufficient to maintain a comparatively large oscillation between (ii) and the Helmholtz resonator. The case when (i) and (ii) are in tune has already been dealt with.

### § 3. *Experimental Results.*

The experiments described in this section illustrate the application of equation (11). Before giving details of the experimental method, it may be well to point out that the theoretical equations are in a form which is suitable for the calculation of the resonant tones of a compound resonator partly from the *frequencies* of its components and partly from their *dimensions*. It is, of course, possible to express the frequencies of the components in terms of their dimensions; but the equations then take on a more complicated form, and the agreement between calculated and observed values would depend not only on the theory given in the present paper, but also on the accuracy of the usual formulæ for calculating the hydrodynamical conductance of an orifice and the correction for an open end. It has been thought best to leave questions as to the accuracy of such formulæ to be answered by special investigations, and to accept the observed frequencies of the components as part of the data for calculating the tones of a compound resonator.

The frequencies of the resonant tones were determined experimentally with the aid of a hot-wire microphone grid mounted in the neck leading from the pipe into the Helmholtz resonator. The resonator to be tested was laid on the ground at a distance of about one metre from an electrically-driven siren of the Seebeck pattern, the speed of which could be controlled by means of a rheostat in series with the armature of the motor. The siren was mounted on a table, and

\* The circumstances here contemplated are, of course, ideal. In practice there is always some loss of energy from the pipe, and the absence of vibration in (ii) would not be complete.

its revolutions per minute were indicated by an Elliot speed-counter attached by flexible shafting to the axle of the motor. The microphone grid formed one arm of a Wheatstone bridge, and the response of the resonator was measured by the deflexion of a microammeter with suitable series and shunt resistances. The deflexion of the microammeter was in all cases very closely proportional to the change in ohmic resistance suffered by the hot-wire grid. The deflexions were observed for a series of selected readings of the speed-counter, and from these readings curves were constructed showing the relation between deflexion and vibrations per second in the fundamental tone of the siren\*. All observations were made out-of-doors.

The error of the speed-counter was found by a stroboscopic method with the help of a tuning-fork, the period of which had been determined from a chronometer by means of a Bull photographic recorder.

The deflexions observed in this method are approximately proportional to the square of the maximum velocity occurring in the neck of the Helmholtz resonator †, that is to

$$\{(1/A) | dq/dt | \}^2,$$

where  $A$  is the cross-sectional area of the neck and  $| dq/dt |$  is the amplitude of the flow in c.c. per second. They are therefore approximately proportional to the *energy* of the vibration in the neck of the resonator. Certain resonant tones, however, would escape notice if this method only were to be relied on, namely those in which  $dq/dt=0$ , as for example those which occur when a Helmholtz resonator is placed at a loop of one of the resonant tones of a stopped pipe. Allowance for this fact must be made in interpreting the experimental results.

A resonator was made similar to that shown diagrammatically in fig. 2. The pipe  $P$  was an iron tube, 10.2 cm. in diameter (internal), and closed at one end by a brass plate .5 cm. thick. The walls of the tube were .6 cm. thick, and the length—measured from the open end to the inside face of the brass plate—was 120.3 cm. The frequency of the fundamental tone of the pipe was determined by ear,

\* The microphone grids and their mounting and the method of plotting "resonance curves" is described in greater detail in Phil. Trans. A, ccxxi. pp. 391-393 & 395-398 (1921). The siren used in the present experiments was of the "circular hole" pattern previously used in the experiments with double resonators described in Proc. Roy. Soc. A, ci. p. 347 (1922).

† Phil. Trans. A, ccxxi. p. 410 (1921). See also R. C. Richards, Phil. Mag. xlv. pp. 926-934 (1923).

the method being as follows:—The pipe was laid on the ground in front of the siren, and the ears of an observer were connected by means of stethoscopes and rubber tubing to a nipple at the closed end of the pipe. The speed of the siren was then gradually increased until the frequency of the note passed through that value at which maximum resonance occurred in the pipe, the observer noting the speed-counter reading when the resonance appeared to him to be loudest. The mean of several observations gave the fundamental frequency of the pipe as  $66\frac{1}{2}$  vibrns. per sec. at  $10^{\circ}\text{C.}$ , and hence the reduced length  $L'$  was 127 cm. (the velocity of sound in air being taken as 337.6 metres per sec. at  $10^{\circ}\text{C.}$ ).

The pipe was provided with brass fittings so that a Helmholtz resonator could be attached at the closed end (as in fig. 1) or in a position  $\frac{1}{4}L'$ ,  $\frac{1}{3}L'$ , or  $\frac{1}{2}L'$  from the closed end, these positions corresponding respectively to the four cases when  $m=1$ ,  $m=\frac{3}{4}$ ,  $m=\frac{2}{3}$ , and  $m=\frac{1}{2}$ . The end of the orifice of the Helmholtz resonator when in position was flush with the inside surface of the wall of the pipe. Two sets of observations were made, the first with a Helmholtz resonator tuned to the fundamental of the pipe, and the second with a resonator tuned to the first overtone of the pipe. The conductance of the orifice was found in each case by attaching it to a container of known volume and measuring the resonance frequency in the usual way with a hot-wire microphone. The conductance was then calculated from the formula

$$c = 4\pi^2 N^2 Q / a^2,$$

$N$  being the resonance frequency,  $Q$  the volume of the container, and  $a$  the velocity of sound.

In the first set of observations, the conductance of the orifice (a cylindrical tube 26.5 mm. long and 6.5 mm. in diameter) was found to be 0.133 cm. So that in equation (11) we have

$$\sigma = \pi(10.2)^2/4 \text{ cm.}^2, \quad c = 0.133 \text{ cm.,}$$

$$\text{and} \quad n_1 = n_0 = 66\frac{1}{2} \text{ vibrns. per sec.}$$

$$\text{Hence} \quad 2\pi\sigma n_1/ac = 7.60.$$

This is sufficiently close to 8 for the intersections of the  $Y_1$  curves with  $AA^1$  in fig. 3 to be used for the purpose of finding approximate values for the frequencies at which resonance peaks should occur in the experimental curves. The approximate values having been found, more exact values are obtained without difficulty by calculating a few

additional points in the neighbourhood of each approximate value. The calculated values of the lower and upper resonance frequencies ( $N_1$  and  $N_2$  vibrns. per sec. respectively) are shown in the second and third columns of Table I. They are given to the nearest half-vibration per second, which is as accurately as they could be determined experimentally. The observed values are shown in the fourth and fifth columns.

TABLE I.

( $n_1 = n_0$ .)

$m$ .	Calculated.		Observed.	
	$N_1$ .	$N_2$ .	$N_1$ .	$N_2$ .
1 .....	54	$80\frac{1}{2}$	$54\frac{1}{2}$	80
$\frac{2}{3}$ .....	55	80	55	$79\frac{1}{2}$
$\frac{5}{3}$ .....	$55\frac{1}{2}$	79	$55\frac{1}{2}$	78
$\frac{1}{2}$ .....	$57\frac{1}{2}$	$76\frac{1}{2}$	$57\frac{1}{2}$	$75\frac{1}{2}$

It will be seen that on the whole the observed values correspond very well with those predicted by theory, although there is evidence of a systematic error in the calculated value of  $N_2$ , this being always  $\frac{1}{2}$  or 1 vibration greater than the observed value. The resonance curves for the cases when  $m=1$  and  $m=\frac{1}{2}$  are reproduced in fig. 4. The curves for  $m=\frac{2}{3}$  and  $m=\frac{5}{3}$  were intermediate in form between those shown in fig. 4, and as  $m$  was increased, the height of the peak due to the upper tone decreased, while that due to the lower tone increased, equality occurring for some value of  $m$  between  $\frac{2}{3}$  and  $\frac{1}{2}$ . It is perhaps somewhat surprising to find that the response is so large when  $m=\frac{1}{2}$ , and some interesting questions arise as to the sensitiveness of instruments made with this type of resonator. A discussion of these questions, however, would necessitate taking into account the losses occurring in the resonator, and would lie outside the scope of the present paper.

The effects to be observed when the Helmholtz resonator is tuned to a note in the region of the first overtone of the pipe are more striking than those just described. The resonator employed in this part of the experiment had an orifice 6.5 mm. in diameter and 21 mm. long. The frequency was 205 vibrns. per sec., and the conductance of the orifice .167 cm., so that we have  $2\pi\sigma n_1/ac=18.7$ . As before, we use the intersection of the  $Y_1$  curves in fig. 3 with the  $Y_2$  curve BB' (which is constructed for the case when



$2\pi\sigma n_1/ac=22$ ) to obtain approximate values of the resonance frequencies, and then find more exact values by calculating a few additional values in the neighbourhood of the approximations, using the proper value of  $2\pi\sigma n_1/ac$ . The calculated and observed frequencies are shown in Table II.

Fig. 4.

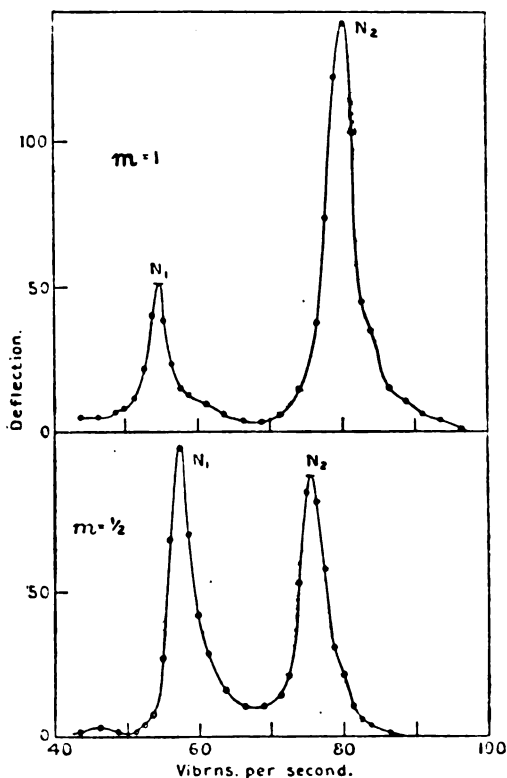
Resonance Curves for Boys Resonator ( $n_1=n_0=66\frac{1}{2}$  vibrs. per sec.).

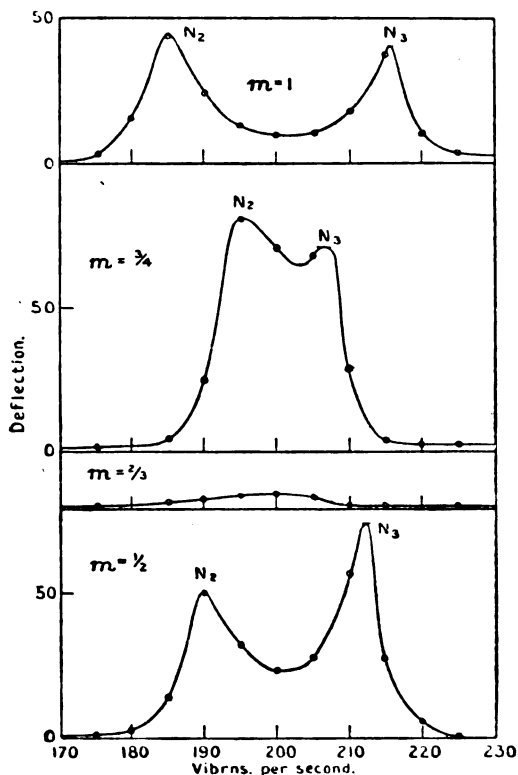
TABLE II.

( $n_1=205$ ,  $n_0=66\frac{1}{2}$ .)

$m$ .	Calculated.		Observed.	
	$N_2$ .	$N_3$ .	$N_2$ .	$N_3$ .
1 .....	186	217	185	216
$\frac{2}{3}$ .....	196	209	195	207
$\frac{3}{2}$ .....	205		200	
$\frac{1}{2}$ .....	191	213	190	212

The agreement here is also satisfactory, although the calculated frequencies are all a little greater than those observed. The resonance curves are shown in fig. 5. It will be seen that the changes in the shape of the curve are

Fig. 5.



Re-onance Curves for Boys Resonator ( $n_1=205$ ,  $n_0=66\frac{1}{2}$ ).

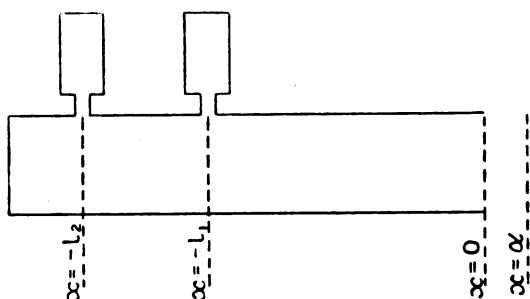
very marked, the most sensitive position for the Helmholtz resonator being when  $m=\frac{3}{4}$ . When  $m=\frac{1}{2}$  the response is very small, the resonator being then at a loop of the first overtone of the pipe.

#### § 4. Combination of a Stopped Pipe with two Helmholtz Resonators.

The kind of resonator dealt with in this section is shown diagrammatically in fig. 6, and is especially useful in the construction of hot-wire microphones which are to be

employed with the bridge method of measurement. In this method, in order to avoid "creeping" of the zero due to changing air-temperature or slow alterations in the battery, it is advisable whenever possible to use two microphone grids—one active and the other compensating—placed in opposite arms of a Wheatstone or battery bridge. If the grids are mounted in the necks of two Helmholtz resonators entering into the same stopped pipe (as in fig. 6), the compensation is very complete, and the arrangement has the additional advantage that when the microphone is used out-of-doors there is some compensation for the disturbing effect of wind.

Fig. 6.



Combination of two Helmholtz Resonators and a Stopped Pipe.

Sensitive microphones of this type have been made for responding to sounds up to 512 vibrations per second, and have been found very effective for measuring the sound reflected and transmitted by partitions of various materials.

In addition to the use indicated above, it will be obvious from what follows that with compound resonators of the type under consideration, microphones can be made which are sensitive to two distinct ranges of frequencies.

It is convenient to begin the theory with the consideration of the more general case of a compound resonator consisting of a number of Helmholtz resonators inserted at intervals in the side of a stopped pipe. For each Helmholtz resonator, say the  $s$ th member of the series (counting from that nearest to the open end of the pipe), let a linear quantity,  $\gamma_s$ , be chosen such that

$$\tan k\gamma_s = \frac{2\pi\sigma}{ac_s} n_s \left( \frac{n}{n_s} - \frac{n_s}{n} \right), \quad \dots \quad (12)$$

where  $n_s$  is the frequency of the  $s$ th resonator (vibrns. per sec.) and  $c_s$  is the conductance of the neck. Thus, if  $\phi_s$  and  $\phi_{s+1}$  be the potentials on each side of the  $s$ th resonator at

$x' = -l'_s$ , we have, corresponding to equations (5) and (8),

$$\sigma \left( \frac{\partial \phi_s}{\partial x'} - \frac{\partial \phi_{s+1}}{\partial x'} \right)_{x'=-l'_s} = \frac{dq_s}{dt}, \quad \dots \quad (13)$$

$$\frac{dq_s}{dt} = \frac{c_s}{1 - (n_s^2/n^2)} \phi_{-l'_s}, \quad \dots \quad (14)$$

Eliminating  $dq_s/dt$  from (13) and (14) and making the substitution indicated in (12), we find that one of the conditions to be satisfied by  $\phi_s$  and  $\phi_{s+1}$  when  $x' = -l'_s$  is

$$\frac{1}{k} \left( \frac{\partial \phi_s}{\partial x'} - \frac{\partial \phi_{s+1}}{\partial x'} \right) = \cot k\gamma_s \cdot \phi_{-l'_s}, \quad \dots \quad (15)$$

while the other is

$$\partial \phi_s / \partial t = \partial \phi_{s+1} / \partial t. \quad \dots \quad (16)$$

If it happens that the  $s$ th resonator is at the closed end of the pipe, that is if  $l'_s = L'$ , then equations (13) and (14) become

$$\sigma \left( \frac{\partial \phi_s}{\partial x'} \right)_{x'=-L'} = \frac{dq_s}{dt}, \quad \dots \quad (17)$$

$$\frac{dq_s}{dt} = \frac{c_s}{1 - (n_s^2/n^2)} \phi_{-L'}, \quad \dots \quad (18)$$

and corresponding to (15) we have

$$\frac{1}{k} \left( \frac{\partial \phi_s}{\partial x'} \right)_{x'=-L'} = \cot k\gamma_s \cdot \phi_{-L'}. \quad \dots \quad (19)$$

Since

$$\phi_s = (A_s \sin kx' + B_s \cos kx') \cos kat, \quad \dots \quad (20)$$

(19) is equivalent to

$$A_s \cos kL' + B_s \sin kL' = \cot k\gamma_s (-A_s \sin kL' + B_s \cos kL'),$$

whence

$$A_s - B_s \cot k(L' + \gamma_s) = 0$$

or

$$A_s \cot k(L' + \gamma_s + \pi/2k) + B_s = 0. \quad \dots \quad (21)$$

Now, if there were no resonator at the closed end of the pipe, the condition to be fulfilled by  $\phi_s$  would be

$$\left( \frac{\partial \phi_s}{\partial x'} \right)_{x'=-L'} = 0, \quad \dots \quad (22)$$

whence

$$A_s \cot kL' + B_s = 0. \quad \dots \quad (23)$$

Comparing (21) with (23), we see that the effect of placing

a resonator at the closed end of the pipe may be represented as the addition of a length  $\Delta L'$  to the reduced length  $L'$ , such that

$$\begin{aligned}\Delta L' &= \gamma_s + (\pi/2k) \\ &= \gamma_s + \frac{1}{4}\lambda. \quad \dots \quad (24)\end{aligned}$$

In terms of the frequencies  $n$  and  $n_s$ ,  $\Delta L'$  is given by the formula :

$$\Delta L' = \frac{a}{2n} \left[ \frac{1}{2} + \frac{1}{\pi} \tan^{-1} \left\{ \frac{2\pi\sigma}{ac_s} n_s \left( \frac{n}{n_s} - \frac{n_s}{n} \right) \right\} \right]. \quad (25)$$

By means of the equations (15), (16), and (21) it is easy to write down the equation, the roots of which will give the frequencies of the resonant tones in any particular case. For example, let there be two Helmholtz resonators, one at  $x' = -l_1'$ , and another at  $x' = -l_2'$ , as in fig. 6. Following the same plan as before, we assume potentials  $\phi_1$  from  $x' = 0$  to  $x' = -l_1'$ ,  $\phi_2$  from  $x' = -l_1'$  to  $x' = -l_2'$ , and  $\phi_3$  from  $x' = -l_2'$  to  $x' = -L'$ , these having the general form for stationary waves given in (20). In addition to the condition at the open end ( $x' = 0$ ), viz.  $\partial\phi_1/\partial t = 0$  so that  $B_1 = 0$ , the conditions to be satisfied by  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  are expressed by (i) two equations of the type (15) and (16) with  $s=1$ ,  $x' = -l_1'$ ; (ii) two similar equations with  $s=2$ ,  $x' = -l_2'$ ; and (iii)  $\partial\phi_3/\partial x' = 0$  when  $x' = -L'$ . Substituting for  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  expressions of the type (20), we thus obtain five equations from which the five constants  $A_1$ ,  $A_2$ ,  $B_2$ ,  $A_3$ , and  $B_3$  can be eliminated. The eliminant is :

$$\begin{vmatrix} -1 & 1 & -\cot kl_1' & 0 & 0 \\ \cot kl_1' + \cot k\gamma_1 & -\cot kl_1' & -1 & 0 & 0 \\ 0 & -1 & \cot kl_2' & 1 & -\cot kl_2' \\ 0 & \cot kl_2' + \cot k\gamma_2 & 1 - \cot k\gamma_2 \cot kl_2' & -\cot kl_2' & -1 \\ 0 & 0 & 0 & \cot kL' & 1 \end{vmatrix} = 0. \quad \dots \quad (26)$$

The values of  $n$ , or  $ka/2\pi$ , which satisfy this equation are the frequencies of the resonant tones. For graphical solution the equation may be written :

$$\frac{\cot kl_2' + T_2 \cot k(L' - l_2')}{1 - S_2 \cot k(L' - l_2')} = \frac{1 + S_1 \cot kl_1'}{S_1 - \cot kl_1'}, \quad (27)$$

where

$$\left. \begin{aligned} S_1 &= \cot kl_1' + \cot k\gamma_1, \\ S_2 &= \cot kl_2' + \cot k\gamma_2, \\ T_2 &= 1 - \cot k\gamma_2 \cot kl_2'. \end{aligned} \right\} \quad \dots \quad (28)$$

In (27) the right-hand side depends only on the position and tuning of the first resonator, while the left-hand side depends on the position and tuning of the second resonator and the reduced length of the pipe. If the second resonator is placed at the closed end of the pipe, *i. e.* if  $l'_2 = L'$ , (27) reduces to

$$-\frac{T_2}{S_2} = \frac{1 + S_1 \cot kl'_1}{S_1 - \cot kl'_1} \quad \dots \quad (29)$$

This result can easily be deduced anew from the equations already given. Thus, instead of three equations expressing the conditions (ii) and (iii) given above, there is in this case one equation of the type (21) with  $s=2$ . With the two equations of condition (i) this makes three equations in all from which the constants  $A_1$ ,  $A_2$ , and  $B_2$  can be eliminated. The result is:

$$\begin{vmatrix} -1 & 1 & -\cot kl'_1 \\ S_1 & -\cot kl'_1 & -1 \\ 0 & \cot k(L' + \Delta L') & 1 \end{vmatrix} = 0, \quad \dots \quad (30)$$

in which  $\Delta L'$  is written for  $\gamma_2 + (\pi/2k)$  and, as before,  $S_1$  for  $\cot kl'_1 + \cot k\gamma_1$ .

Since  $\cot k(L' + \Delta L') = S_2/T_2$ , (30) is easily seen to be identical with (29).

Alternatively (30) can be written

$$\frac{1}{\cot kl'_1 - \tan k(L' + \Delta L' - l'_1)} = -\tan k\gamma_1, \quad \dots \quad (31)$$

a form which could have been obtained immediately from (10) by writing  $L' + \Delta L'$  in place of  $L'$ . The equation corresponding to (11) is

$$\frac{1}{\cot(m\pi n/2n_0) - \tan[\{(1-m)\pi n/2n_0\} + \epsilon + (\pi/2)]} = -\frac{2\pi\sigma}{ac_1} n_1 \left( \frac{n}{n_1} - \frac{n_1}{n} \right), \quad (32)$$

where

$$\epsilon = \tan^{-1} \left\{ \frac{2\pi\sigma}{ac_2} n_2 \left( \frac{n}{n_2} - \frac{n_2}{n} \right) \right\} \dots \quad (33)$$

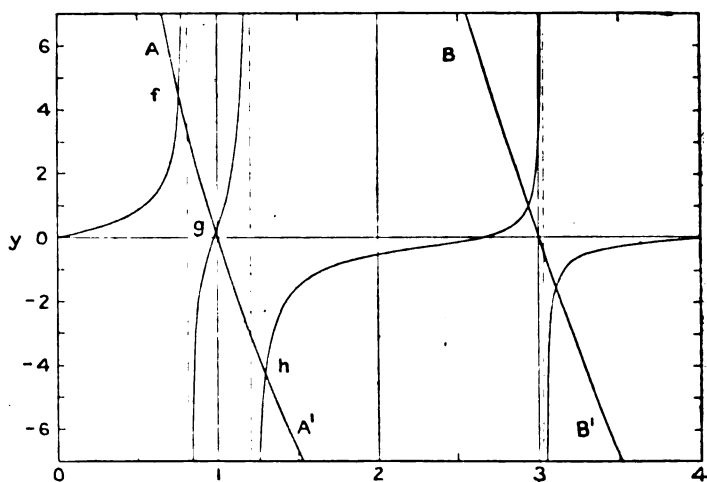
As an example of the use of these equations, we will consider the determination of the frequencies of the resonant tones by a graphical solution of (32). Let  $m = \frac{3}{4}$ ,  $n_2 = n_0$ ,

788 Dr. E. T. Paris : *Determination of Frequencies of*  
and  $(2\pi\sigma/ac_2)n_2=8$ . We first plot the values of

$$Y_1 = \frac{1}{\cot(m\pi n/2n_0) - \tan[\{(1-m)\pi n/2n_0\} + \epsilon + (\pi/2)]} \quad (34)$$

against  $n/n_0$ . The resulting curve is shown in fig. 7 as far as  $n/n_0=4$ . As in the case of a stopped pipe with only one Helmholtz resonator (fig. 3), the curve is divided into a number of branches by asymptotes perpendicular to the axis  $y=0$ . These are shown by the broken lines in fig. 7. The

Fig. 7.



Graphical Solution of Equation (32).

position of the asymptotes is determined by the condition that the denominator of the right hand of (34) is equal to zero : i. e.,

$$\cot(m\pi n/2n_0) = \tan[\{(1-m)\pi n/2n_0\} + \epsilon + (\pi/2)],$$

from which we find that the condition is

$$\tan(\pi n/2n_0) = -\tan \epsilon,$$

or, by (33),

$$\tan \frac{\pi n}{2n_0} = -\frac{2\pi\sigma}{ac_2} n_2 \left( \frac{n}{n_2} - \frac{n_2}{n} \right).$$

Now, the values of  $n$  which satisfy this equation are the frequencies of the resonant tones of the Boys resonator made from the pipe and the second resonator ( $n_2$ ) alone (see equation (1)). Therefore the asymptotes of the  $Y_1$  curve are the

lines  $n/n_0 = \mu_1$ ,  $n/n_0 = \mu_2$ , etc., where  $\mu_1$ ,  $\mu_2$ , etc., are such that  $\mu_1 n_0$ ,  $\mu_2 n_0$ , etc., are the resonance frequencies of the Boys resonator at  $x = -l_1'$ . Comparing this with the case discussed in the previous section, we see that the asymptotes in fig. 7 perform precisely the same rôle as do the asymptotes at  $n/n_0 = 1, 3$ , etc., in the simple case of a pipe combined with one resonator. In the latter case the asymptotes cut the axis  $y=0$  at values of  $n/n_0$ , which give the frequencies of the stopped pipe alone.

As before, if  $m$  has certain values, the orifice of the resonator  $n_1$  may be at a loop of the vibration within the pipe. This happens if  $m$  is such that  $mL' = \alpha/2\mu_n n_0$ , where  $\mu_n n_0$  is one of the resonance frequencies of the Boys resonator made from the pipe and the end resonator alone. Since  $L'$  must exceed half a wave-length in order that a loop may occur within the pipe,  $\mu_n$  must be greater than 2.

The line  $AA'$  (fig. 7) is the curve found by plotting

$$Y_2 = -\frac{2\pi\sigma}{ac_1} n_1 \left( \frac{n}{n_1} - \frac{n_1}{n} \right)$$

against  $n/n_0$  for the case when  $n=n_0$  and  $2\pi\sigma n_1/ac_1=8$ . There are now three intersections with the  $Y_1$  curve in the neighbourhood of  $n_0$ , at  $f$ ,  $g$ , and  $h$  (fig. 7). In addition there are intersections (not shown in the figure) which give the frequencies of the overtones of the combination. The curve  $BB'$  illustrates the case when the resonator  $n_1$  is tuned to the first overtone of the pipe. There are now two resonant tones in the neighbourhood of  $3n_0$  and two in the neighbourhood of the fundamental  $n_0$ . The intersections indicating the latter are not shown in the figure.

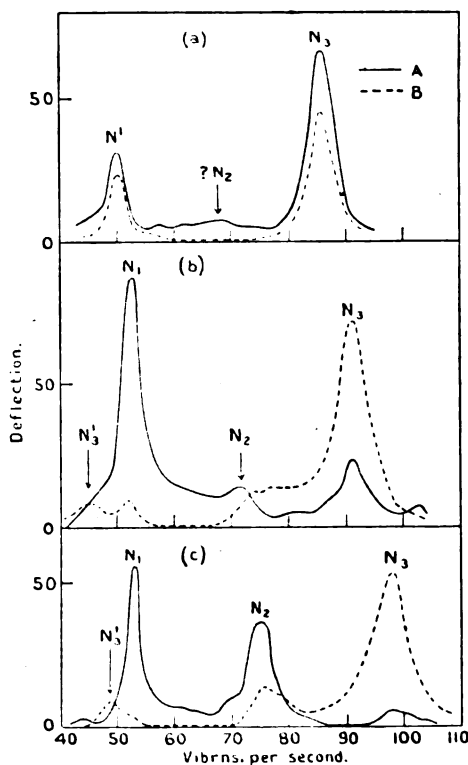
### § 5. Experiments with a Stopped Pipe and two Helmholtz Resonators.

The pipe used in these experiments was the same as that employed in the experiments described in § 3. One Helmholtz resonator (A) was placed at the stopped end of the pipe and another (B) in the side of the pipe. The resonator A was the same as that employed in the previous experiments, and was tuned to the fundamental of the pipe, so that in equation (33), which is subsidiary to (32), we have  $n_2=66\frac{1}{2}$  vibrns. per second,  $c_2=0.133$  cm., and  $2\pi\sigma n_2/ac_2=7.60$ . The resonator B was at a distance of one quarter of the reduced length of the pipe from the stopped end, so that in equation (32) we have  $m=\frac{3}{4}$ . Several experiments were made with different tunings of the resonator B, and the



results of three of them are shown in fig. 8. In each case there are two curves, one plotted from a hot-wire grid in A's orifice, and one from a hot-wire grid in B's orifice. These are shown in fig. 8 by the full and broken lines respectively\*.

Fig. 8.



Resonance Curves for Combination of Stopped Pipe and two Helmholtz Resonators (A and B).

In the first experiment the frequency of B was  $64\frac{1}{2}$  vibrns. per second and the conductance of its orifice 0.127 cm., so that  $2\pi\sigma n_1 l a c_1 = 7.72$  in equation (32). For this tuning of B an inspection of fig. 7 shows that there should be three resonant tones, the exact values of the frequencies to be

\* For the sake of clearness, observed points are not plotted in the figure, there being from forty to fifty points on each curve.

expected being shown under  $N_1$ ,  $N_2$ , and  $N_3$  in Table III. The resonance curves are shown at (a) (fig. 8), and it will be seen that, although  $N_1$  and  $N_3$  are well marked, the central tone  $N_2$  is only feebly indicated in the curve for the resonator A, and probably not at all in the curve for the resonator B.

When the frequency of B is raised, however, the energy of the vibration at  $N_2$  in the A resonator grows at the expense of those at  $N_3$  in A and  $N_1$  in B. This is shown by the curves at (b) (fig. 8). The tuning of B was here such that  $n_1=81$  vibrns. per sec.,  $c_1=0.127$  cm., and  $2\pi\sigma n_1/ac_1=9.70$ . The small peak at  $N_3'$  is due to the impurity of the siren note, and is the response of B to the octave of the fundamental siren tone.

If the frequency of B is still further raised, the same process continues. The curves shown at (c) (fig. 8) are for the case when  $n_1=93$  vibrns. per sec.,  $c_1=0.127$  cm., and  $2\pi\sigma n_1/ac_1=11.1$ . The vibration at  $N_2$  in the A resonator is still more pronounced, while that at  $N_3$  is inconsiderable. Similarly, practically all the energy in the B curve is concentrated into the peak at  $N_3$ . In this case also, B responds to the octave of the siren note at  $N_3'$ .

When  $n_1$  is in the region of the first overtone of the pipe, the A curve is practically the same as that for  $m=1$  in fig. 4, and the B curve is nearly that for  $m=\frac{3}{2}$  in fig. 5. This was shown by an experiment in which  $n_1=205$  vibrns. per sec., and  $c_1=0.167$  cm. The resonance curves for this experiment are not reproduced, but the observed and calculated resonance frequencies are included in Table III.

TABLE III.

( $n_2=n_0=66\frac{1}{2}$ .)

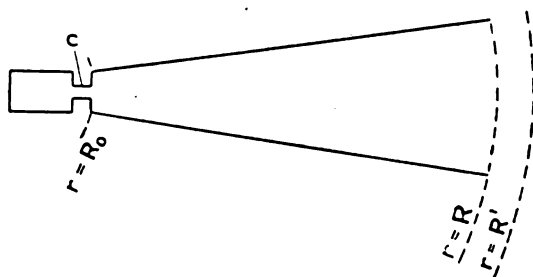
	$\frac{2\pi\sigma n_1}{ac_1}$	Calculated.			Observed.		
		$N_1$	$N_2$	$N_3$	$N_1$	$N_2$	$N_3$
$64\frac{1}{2}$ .....	7.72	50	$65\frac{1}{2}$	86	50	$767\frac{1}{2}$	$85\frac{1}{2}$
81 .....	9.70	$52\frac{1}{2}$	$72\frac{1}{2}$	92	$52\frac{1}{2}$	$71\frac{1}{2}$	91
93 .....	11.1	$52\frac{1}{2}$	76	$90\frac{1}{4}$	53	75	98
205 .....	18.7	$53\frac{1}{2}$	79	197	54	$79\frac{1}{4}$	194

In the case when  $n_1=205$ , the fourth tone ( $N_4$ ) was observed at 206 vibrns. per second, corresponding to a calculated value of 210 vibrns. per second.

§ 6. *Combination of Helmholtz Resonator and Conical Horn.*

Compound resonators consisting of a Helmholtz resonator combined with a conical horn have been used for the purpose of producing sensitive hot-wire microphones. A simple arrangement of this kind is shown diagrammatically in fig. 9. If the horn is made sufficiently large compared with the wave-length of the incident sound, the instrument is directive in its action, the greatest response being obtained when the mouth of the horn is directed towards the source of sound. If, however, the mouth of the horn is less than half a wave-length in diameter, the directive action is not very marked, and the sensitivity of the instrument appears to depend on the resonant properties of the combination rather than on the sound-collecting power of the conical horn.

Fig. 9.



Conical Horn and Helmholtz Resonator.

No attempt will be made in the present paper to give a complete theory of this type of instrument, but attention will be confined to methods of calculating the resonance frequencies in the special case when the directive properties are not well marked—that is, when the diameter of the conical horn can be treated as small compared with the wave-length. Some modifications of the simple form of resonator shown in fig. 9 will also be dealt with.

The theory of this type of resonator probably shows many similarities to that of such instruments as the phonodeik of D. C. Miller \* and the Low-Hilger "audiometer" †. The essential feature of these instruments—which are primarily

\* 'The Science of Musical Sounds,' pp. 78-87. (1916).

† Alias the "Optical Sonometer." See F. Twyman and J. H. Dowell, Journ. of Sci. Instruments, Preliminary Number, pp. 254-255 (May, 1922).

intended for the examination of wave-form—is a light diaphragm mounted near the vertex of a conical horn. The diaphragm and horn form a compound resonator, analogous to that consisting of a horn and Helmholtz resonator, which generally exhibits very pronounced resonance frequencies.

The first arrangement to be considered is that shown in fig. 9. The conical horn is truncated at the narrow end and closed by a flat plate, through a hole in which is inserted the orifice of the Helmholtz resonator.

In order to find the resonant tones, we assume a stationary vibration of the air within the cone. If the vertex of the cone is taken as the origin, the general expression for the stationary vibration is

$$\phi = \frac{1}{r} (A \sin kr + B \cos kr) \cos kat, \quad \dots (35)$$

where  $r$  is the distance measured from the vertex. Let the closed end of the cone be at  $r=R_0$  (see fig. 9) and the open end at  $r=R$ , and let  $R'=R+\alpha$ , where  $\alpha$  is the end correction. Also let  $L'=R'-R_0$ .

The condition to be satisfied by  $\phi$  at the open end is

$$(\partial\phi/\partial r)_{r=R'} = 0,$$

whence

$$B = -A \tan kR',$$

so that

$$\begin{aligned} \phi &= (A/r)(\sin kr - \tan kR' \cos kr) \cos kat \\ &= (A \sec kR'/r) \sin k(r-R') \cos kat. \quad \dots (36) \end{aligned}$$

The condition to be satisfied at the closed end of the pipe is that the total flux across a portion of spherical surface of radius  $R_0$  drawn inside the pipe is equal to the total flux into the Helmholtz resonator. If  $\Omega$  is the solid angle of the cone, this condition is expressed by the equation :

$$\left\{ \Omega r^2 \frac{\partial \phi}{\partial r} \right\}_{r=R_0} = \frac{dq}{dt} \quad \dots (37)$$

Finally, if  $c$  is the conductance of the neck of the Helmholtz resonator and  $Q$  is its volume, we have

$$\frac{dq}{dt} = c(\phi_{R_0} - \psi), \quad \psi = (a^2/Q) \int q dt. \quad \dots (38)$$

Putting  $4\pi^2 n_1^2 = a^2 c/Q$ , we have, from (38),

$$\frac{dq}{dt} = \frac{c}{1 - (n_1^2/n^2)} \phi_{R_0}. \quad \dots (39)$$

Whence, eliminating  $dq/dt$ ,

$$\left\{ \Omega r^2 \frac{\partial \phi}{\partial r} \right\}_{r=R_0} = \frac{c}{1 - (n_1^2/n^2)} \phi_{R_0} \quad \dots (40)$$

It is evident from (40) that in the expression for  $\phi$  given in (36) we may put  $A \sec kR'$  equal to unity, so that the potential inside the cone may be taken to be

$$\phi = (1/r) \sin k(r - R') \cos kat. \quad \dots (41)$$

Substituting this value of  $\phi$  in (40), we obtain, as the equation for the frequencies of the resonant tones,

$$\Omega \{ \sin kL' + kR_0 \cos kL' \} = - \frac{c}{1 - (n_1^2/n^2)} \frac{\sin kL'}{R_0}$$

or

$$\frac{1}{1 + kR_0 \cot kL'} = - \frac{\Omega R_0}{c} \left( 1 - \frac{n_1^2}{n^2} \right). \quad \dots (42)$$

Whence, corresponding with equation (1), § 2,

$$\frac{1}{(a/2\pi n R_0) + \cot(2\pi n L'/a)} = - \frac{2\pi \Omega R_0^2}{ac} n_1 \left( \frac{n}{n_1} - \frac{n_1}{n} \right). \quad (43)$$

The length  $L'$  is an acoustical length, and includes an end-correction which varies with the solid angle of the cone. The frequency equation for a cone closed at  $r=R_0$  is

$$\tan kL' + kR_0 = 0. \quad \dots (44)$$

So that, if  $n_0$  is the observed fundamental frequency of the cone, we have

$$L' = \frac{a}{2\pi n_0} \left\{ \tan^{-1} \left( - \frac{2\pi n_0 R_0}{a} \right) \right\}. \quad \dots (45)$$

From (43) we easily return to the case of the Boys double resonator, with a parallel pipe. (43) is, in fact, more general than equation (1), § 2, and includes the parallel pipe as a special case. In order to return to the case of the parallel pipe, let  $\Omega \rightarrow 0$  and  $R_0 \rightarrow \infty$  in such a way that the product  $\Omega R_0^2$  remains finite and equal to the cross-sectional area at the closed end of the pipe. In these circumstances the first term in the denominator of the left side of (43) becomes negligible, and the equation may be rewritten in the form

$$\tan \frac{2\pi n L'}{a} = - \frac{2\pi \sigma}{ac} n_1 \left( \frac{n}{n_1} - \frac{n_1}{n} \right). \quad \dots (46)$$

At the same time  $L'$  becomes equal to  $a/4n_0$  in accordance with (45), so that (46) is wholly equivalent to equation (1).

The solution of (43) may be effected graphically, as in the case of (11) and (32). As with the parallel pipe (fig. 3,  $m=1$ ), the  $Y_1$  curve, representing the left-hand side of (43), is divided into a number of branches by asymptotes perpendicular to the line  $y=0$ , these cutting it at points corresponding to the resonance frequencies of the cone without the Helmholtz resonator. The curve is non-periodic owing to the presence of the term  $a/2\pi nR_0$  in the denominator of  $Y_1$ . A numerical example of the solution of (43) is given in § 7.

If the resonator is placed so that its orifice enters through the side of the conical pipe an equation for the resonant tones can be deduced analogous to (11), § 2. This case is of some practical importance, since an attempt has been made to use auxiliary resonators in this way in order to remove objectionable resonances from conical horns such as those used in "loud-speakers" and gramophones\*.

Let  $R_1$  be the distance of the orifice of the resonator from the vertex, and let  $R_0$  and  $R'$  have the same meanings as before. Also let  $\phi_1$  and  $\phi_2$  be potentials of the general form (35),  $\phi_1$  being the potential from  $r=R'$  to  $r=R_1$ , and  $\phi_2$  the potential from  $r=R_1$  to  $r=R_0$ . From the condition that  $\partial\phi_1/\partial t=0$  when  $r=R'$  and  $r^2(\partial\phi_2/\partial r)=0$  when  $r=R_0$ , we find that suitable expressions for  $\phi_1$  and  $\phi_2$  are

$$\left. \begin{aligned} \phi_1 &= -\frac{1}{r} \frac{A}{\cos kR'} \sin k(R'-r) \cos kat, \\ \phi_2 &= +\frac{1}{r} \frac{A_2}{\sin k(R_0+\rho_0)} \cos k(r-R_0-\rho_0) \cos kat, \end{aligned} \right\} \quad (47)$$

where  $\rho_0$  is a linear quantity such that  $\cot k\rho_0=kR_0$ .

The conditions to be satisfied when  $r=R_1$  are

$$\left. \begin{aligned} \partial\phi_1/\partial t &= \partial\phi_2/\partial t, \\ \Omega r^2 \left( \frac{\partial\phi_1}{\partial r} - \frac{\partial\phi_2}{\partial r} \right) &= \frac{c}{1-(n_1^2/n^2)} \phi_{R_1}. \end{aligned} \right\} \quad (48)$$

From the first of these conditions we find that

$$A_2 = -\frac{\sin k(R'-R_1) \sin k(R_0+\rho_0)}{\cos kR' \cos k(R_1-R_0-\rho_0)} A_1,$$

\* I am indebted for this information to Mr. P. Rothwell. The work is referred to in a letter to 'Nature,' Feb. 24th, 1923, pp. 254-255, but a full account has not been published.

so that the expressions for  $\phi_1$  and  $\phi_2$  may now be written,

$$\left. \begin{aligned} \phi_1 &= -\frac{1}{r} \sin k(R' - r) \cos kat, \\ \phi_2 &= +\frac{1}{r} \frac{\sin k(R' - R_1)}{\cos k(R_1 - R_0 - \rho_0)} \cos k(r - R_0 - \rho_0) \cos kat. \end{aligned} \right\} \quad (49)$$

By substituting these values in the second of conditions (48) and rearranging the terms, we obtain the equation for determining the resonant tones in the standard form,

$$\cot k(R' - R_1) - \tan k(R_1 - R_0 - \rho_0) = -\frac{2\pi\Omega R_1^2}{ac} n_1 \left( \frac{n}{n_1} - \frac{n_1}{n} \right). \quad (50)$$

As a check on this result we may note that if  $R_1$  is put equal to  $R_0$ , (50) becomes identical with (43).

If, instead of being truncated at  $r=R_0$  the cone is continued as far as the vertex, we have  $R_0=0$ , and hence

$$k\rho_0 = \cot^{-1}(kR_0) = \pi/2,$$

so that (50) becomes

$$\cot k(R' - R_1) + \cot kR_1 = -\frac{2\pi\Omega R_1^2}{ac} n_1 \left( \frac{n}{n_1} - \frac{n_1}{n} \right). \quad (51)$$

One other arrangement may be noted—namely, that made by placing one Helmholtz resonator at  $r=R_1$  and another at  $r=R_0$ , the cone being closed at  $r=R_0$  except for the orifice of the resonator. Let  $n_1$  be the frequency and  $c_1$  the conductance of the orifice of the resonator at  $r=R_1$ , and  $n_2, c_2$  the frequency and conductance of the orifice of the one at  $r=R_0$ . Let  $\phi_2$  be the potential between  $r=R_1$  and  $r=R_0$ . If the cone were completely closed at  $r=R_0$ , the condition to be satisfied by  $\phi_2$  would be

$$\left\{ \Omega r^2 \frac{\partial \phi_2}{\partial r} \right\}_{r=R_0} = 0. \quad (52)$$

Whence, since

$$\phi_2 = (1/r)(A_2 \sin kr + B_2 \cos kr) \cos kat,$$

$$A_2 \cot k(R_0 + \rho_0) - B_2 = 0, \quad (53)$$

where, as before,  $\rho_0$  is a linear quantity such that

$$\cot k\rho_0 = kR_0.$$

When there is a resonator at  $r=R_0$ , we have, instead of (52),

$$\left\{ \Omega r^2 \frac{\partial \phi_2}{\partial r} \right\}_{r=R_0} = \frac{c}{1 - (n_2^2/n^2)} \phi_{R_0}, \quad \dots \quad (54)$$

from which we find

$$\begin{aligned} & A_2(1 - kR_0 \cot kR_0) + B_2(\cot kR_0 + kR_0) \\ &= -\frac{c_2}{1 - (n_2^2/n^2)} \frac{1}{\Omega R_0} (A_2 + B_2 \cot kR_0). \quad \dots \quad (55) \end{aligned}$$

Let

$$\cot k\gamma = \frac{c_2}{1 - (n_2^2/n^2)} \frac{1}{\Omega k R_0^2}.$$

Then (55) may be rewritten in the form,

$$\begin{aligned} & A_2 \{1 - kR_0 (\cot kR_0 + \cot k\gamma)\} \\ &+ B_2 \{kR_0 + (\cot kR_0 + kR_0 \cot kR_0 \cot k\gamma)\} = 0, \\ &\text{or} \quad A_2 \cot k\mathfrak{K} - B_2 = 0, \quad \dots \quad (56) \end{aligned}$$

where

$$\cot k\mathfrak{K} = \frac{kR_0 (\cot kR_0 + \cot k\gamma) - 1}{kR_0 + \cot kR_0 + kR_0 \cot kR_0 \cot k\gamma}. \quad \dots \quad (57)$$

Comparing (56) with (53), we see that the equation for determining the resonant tones can be found by writing  $\mathfrak{K}$  in place of  $(R_0 + \rho_0)$  in (50). If  $kR_0$  is small, we have approximately

$$kR_0 \cot kR_0 = 1,$$

and in this case

$$\cot k\mathfrak{K} = \cot k(\Gamma + \rho_0) \quad \dots \quad (58)$$

if

$$\cot k\Gamma = \cot kR_0 + \cot k\gamma.$$

In the application of equations (50), (51), and similar forms it is necessary to bear in mind that if  $R_1$  has certain values, the Helmholtz resonator in the side of the cone may be situated at a loop of one of the overtones of the cone, or



cone and resonator combination. The remarks in § 2 concerning the effect on the position of the resonant tones when the Helmholtz resonator is at a loop of one of the overtones of a parallel pipe apply *mutatis mutandis* to the case of the conical pipe.

### § 7. *Experiment with Conical Horn and Helmholtz Resonator.*

In order to test equation (43), a conical horn was made from "Fibre Sheet" about 1 mm. thick. The slant length of this horn was 122 cm., the diameter of the wide end 30.5 cm., and of the narrow end 10.6 cm., so that  $R_0 = 65$  cm. The narrow end of the horn was closed with a flat plate of brass, into the middle of which could be screwed the neck of a Helmholtz resonator,

The fundamental resonance frequency ( $n_0$ ) of the cone was found to be  $99\frac{1}{2}$  vibrns. per sec. Putting these values of  $n_0$  and  $R_0$  in (45), we find that  $L' = 132$  cm.

Two experiments were performed. In the first one a Helmholtz resonator of frequency  $93\frac{1}{2}$  vibrns. per sec., with an orifice of conductance .127 cm., was attached to the cone. We have in this case  $2\pi\Omega R_0^2/ac = 12.1$ , the air-temperature at the time of the experiment being  $4^{\circ}5$  C. The resonance frequencies in the neighbourhood of the fundamental calculated from (43) are 84 and 101 vibrns. per sec. The observations showed that there was one resonant tone of frequency 87 vibrns. per sec. and another of frequency between 98 and 103 vibrns. per sec. There was some doubt as to the exact position of the upper tone, since the upper peak in the resonance curve was not of a simple kind, but was itself divided into two peaks, one at 98 and the other at 103 vibrns. per sec. It seemed probable that this was due to a vibration in the wall of the horn, which was of a somewhat flimsy nature.

In the second experiment a Helmholtz resonator tuned to 205 vibrns. per sec., with an orifice of conductance .167 cm., was used. This frequency is close to the first overtone of the horn, namely about 210 vibrns. per sec. The frequencies at which resonance would be expected to occur, calculated from (43), are 192 and 218 vibrns. per sec., while the observed frequencies were 190 and 215 vibrns. per sec.

These results are sufficient to show that equation (43) is

substantially true, although (for the reason stated) the agreement between the calculated and observed values in the first part of the experiment was not very satisfactory.

### § 8. *Summary.*

Theoretical expressions are obtained by means of which the resonance frequencies of several types of compound resonator employed in acoustical instruments can be calculated by the use of graphical methods. The types of resonator discussed are :—

(1) The Boys double resonator, consisting of a Helmholtz resonator combined with a stopped pipe. The theory previously given is extended to the case when the Helmholtz resonator is at some distance from the stopped end of the pipe, and the relation between the resonance frequencies and the distance of the Helmholtz resonator from the stopped end is discussed. This type of resonator is used in the Rayleigh disk and hot-wire instruments.

(2) A compound resonator made from two Helmholtz resonators and a stopped pipe. This kind of resonator is used in hot-wire microphones which are to be employed with the "bridge" method of measurement, or which are to be sensitive throughout two distinct ranges of frequencies.

(3) A combination of Helmholtz resonator and conical horn used for hot-wire microphones, and analogous to the diaphragm and horn combination in the phonodeik and similar instruments.

Experiments are described which show a satisfactory agreement with the theoretical results.

### § 9. *Conclusion.*

The work described in this paper was performed in the Acoustical Research Section of the Signals Experimental Establishment, Woolwich, and is one of the investigations carried on in that Section with the assistance of the Department of Scientific and Industrial Research.

Signals Experimental Establishment,  
Woolwich,  
May 1924.

LXXIX. *Studies on the Deformation of Tungsten Single Crystals under Tensile Stress.* By The Research Staff of the General Electric Co., Ltd.\* (*Work conducted by F. S. GOUCHER.*)

[Plates XVI.-XXIV.]

*Summary.*

A COMBINED X-ray and microscopic study is made of the deformed single crystals—in particular the fractured crystals—which are produced by the extension and fracture of fine tungsten wires composed of crystals, many of which occupy locally the complete volume of the wire.

The deformation may be accounted for in all cases by slip on the (112) planes and in the [111] direction, with the single exception of a crystal subject to special constraints which slipped as well on the (100) planes and in the [100] direction. The [111] direction represents the line of densest packing of atoms for this type of lattice structure—the body-centred—the [100] direction being next in order. The results are therefore in accord with the direction of easiest slip in the case of single crystals of metals involving other types of lattice.

Marked distortions of the crystal planes occur in the direction of slip equivalent to changes in inclination of the plane to this direction of from  $10^{\circ}$ – $20^{\circ}$  without any corresponding change in the atomic spacing; which leads to the view that such distorted crystals are no longer “single crystals” in the strict sense, and that such distortion is the cause of hardening due to slip.

The most favourable crystal orientation for extension by slip is such that two sets of 112 planes are symmetrical to the stress, each making an angle of  $35^{\circ}$  with the direction of stress; in agreement with the most prevalent orientation in drawn tungsten wires and rolled tungsten foils.

The most favourable orientation for slip on one set of planes is about  $40^{\circ}$  to the direction of stress, which accounts for the stability of crystal orientation when two sets of (112) planes are symmetrical to the stress.

(1) *Introduction.*

IN a previous paper † experiments were described dealing with the strength of tungsten single crystals under such conditions that the crystals always fractured in the form of wedges approximately symmetrical to the axis of the specimen and the direction of stress. This condition was obtained by the use of fine wires, so treated that many crystals

\* Communicated by the Director.

† Phil. Mag. Aug. 1924, p. 229.

occupied locally the complete volume of the wire. On submitting such wires to tensile stress, deformation occurred only in certain of these large crystals, and chance ensured that at least one of these would have an orientation very near to that offering the minimum resistance to deformation and fracture.

It was shown by means of X-ray analysis that the crystals after deformation were still single crystals, and that the crystal orientation was the same within  $10^\circ$  for all fractured crystals. It was assumed that, in common with single crystals of other metals, viz. aluminium\*, zinc†, and tin‡, deformation takes place by a process of slip on definite crystal planes. The crystal orientation with respect to the symmetrical wedge forms was such that the (112) planes were indicated as the slip planes, the direction of slip being the [111] direction. It was stated that experiments were in hand which definitely established this. It is the object of the present paper to describe these experiments. They include, in addition to a further study of the crystal forms by means of X-rays, a microscopic study of the etching pits produced in these crystals which throws some light on the mechanism of their deformation.

Information in regard to the exact mechanism of deformation of these crystals is desirable because of the interpretation of the strength measurements and their co-ordination with other physical properties as already described. Further, the determination of the slip plane and direction of slip is of interest because as yet no such determination has been made in the case of a metal having the body-centred type of lattice structure.

## (2) *The Crystal Forms.*

The crystal forms studied were the fractured crystal wedges and the deformed crystals produced in the fractured wires in the manner described in detail in the previous paper. To minimize the experimental difficulties of X-ray analysis, angle measurements, and microscopic examination, only the largest wires—0.20 mm. in diameter—were used. The temperature at which these wires were fractured was about  $3000^\circ$  K. unless otherwise stated, the stress being about 1 kg./mm.<sup>2</sup> and the time of fracture about 1 minute.

Photographs showing exterior views of typical crystal

\* G. I. Taylor and C. F. Elam, *Proc. Roy. Soc. A*, vol. cii. p. 643 (1923).

† Mark, Polanyi, Schmid, *Zeit. f. Phys.* xii. (1922).

‡ Mark, Polanyi, *Zeit. f. Phys.* xviii. (1923).

forms are shown in figs. 1-3 (Pl. XVI.), taken at a magnification of 50. Figs. 1 and 2 show two views of the same wire in perpendicular directions. They show a markedly symmetrical wedge-shaped fracture, and a partially formed wedge, slightly asymmetrical to the wire axis. It is to be noted that the edge of the wedge shown in fig. 2 is not a true representation of the form of this edge because at the moment of fracture an arc takes place—the wire being heated electrically—causing the metal near the end of the wedge to melt. Fig. 3 shows another wedge form often obtained; such wedges are shorter than those shown in figs. 1 and 2 and have a larger wedge angle.

Etched sections of such wires cut parallel to the wire axis so as to show the wedge forms are shown in figs. 4, 5, and 6, taken at a magnification of 70. The specimens were mounted in hard glass which has a coefficient of expansion very nearly equal to that of tungsten, and which has the advantage that the specimen can be seen during the course of grinding. The etching was carried out in boiling hydrogen peroxide, the etching time being two minutes. Fig. 4 shows a typical long wedge slightly asymmetrical; fig. 5 a partially formed wedge; and fig. 6 a typical short wedge such as that shown in fig. 3. In all cases it is clear that deformation has taken place in large crystals occupying the full wire diameter.

These crystal forms suggest that deformation has taken place by a process of slip on crystal planes in all cases, and in the particular case shown in fig. 5 it appears to have occurred almost entirely on one set of planes perpendicular to the plane of the section.

### (3) *Direct Determination of Slip Plane and Direction of Slip.*

Since the direction of slip and the inclination of the slip plane can be directly measured in the case of certain forms, it only remains to determine the crystal orientation by means of X-ray analysis in order to identify the slip plane and the direction of slip for this particular case.

Such a determination has been made for the crystal form shown in the photograph (fig. 7, Pl. XVII.) ( $\times 50$ ); the plane of slip is practically perpendicular to the plane containing the wire axis and the direction of slip, and the inclination of this plane to the wire axis is very nearly  $40^\circ$ .

The wire was mounted in hard glass as before, and a section cut as nearly as possible through the slipped portion of the crystal; this section was an elongated ellipse with its major axis inclined at about  $7^\circ$ —determined by careful measurement—to the direction of slip, and its minor axis

approximately perpendicular to the wire axis and the direction of slip. A determination of the crystal orientation with respect to the plane of this section was made by means of an X-ray spectrometer (such as that used in the measurements described in the previous paper).

The results of this analysis show that a set of (112) planes is inclined to the plane of the section at very nearly the same angle as the measured plane of slip. These (112) planes are, however, distorted; the nature of the distortion is such as to affect the inclination of the planes, but not apparently the atomic spacing. There is no variation in inclination of these planes in directions parallel to the minor axis of the section, but there is a variation in the direction of the major axis. The mean inclination of these planes with respect to the direction of the major axis was found to be  $6^\circ$ , and the inclination of these planes with respect to the minor axis was about  $2^\circ$ , which agrees very well with the inclination of the measured plane of slip to these two directions. It is therefore considered as established that the (112) planes are the planes of slip in this case.

Some of the X-ray photographs used in the determination are shown in fig. 8, Nos. II, III, and IV (Pl. XVII.). They were taken with a small Debye camera—3 cm. radius,—the specimen being mounted at the axis which was perpendicular to the direction of the X-ray beam. No. I shows the positions of (110), (100), and (112) reflexions, obtained from undistorted crystals, when the corresponding planes approximately intersect the spectrometer axis, and is merely given as a standard of reference. No. II shows a (112) reflexion obtained with the specimen in question mounted so that its minor axis intersects the spectrometer axis; it shows a spot of normal size and pattern characteristic of an undistorted crystal. No. III shows the corresponding reflexion obtained when the major axis of the specimen intersects the spectrometer axis; the reflected spot is markedly elongated. Such a spot is equivalent to the effect of gradually inclining an undistorted crystal to the spectrometer axis through an angle of about  $10^\circ$ , as calculated from the constants of the spectrometer. No. IV shows the effect of actually inclining the minor axis from its position as shown in II to one making an angle of  $10^\circ$  with the spectrometer axis. The distortion giving rise to the elongation need not, of course, be a uniform bending, and preliminary measurements on this point indicate that it is not, but rather of the nature of a buckling up of the planes in the direction of slip.

The direction of slip along such a (112) plane was not determined in the case of this crystal, but other crystals having exactly the same form were examined for crystal orientation by cutting sections perpendicular to the slip plane and parallel to the wire axis, and examining them in the X-ray spectrometer. A number of these were studied, and all showed a (110) set of planes to be within a few degrees parallel with such a section. This limits the direction of slip to the  $[111]$  direction, viz. along the diagonal of the unit cube of the tungsten lattice. The dimensions referred to are more easily visualized by reference to the photographs of the model shown in figs. 9 and 10 (Pl. XVIII.). Fig. 9 shows the arrangement of atoms in a unit cube of the tungsten lattice which is of the body-centred type. The vertical plane of the model is a (110) plane, viz. the plane passing through atoms 1 2 3 4 5. A (112) plane is a plane passing through atoms 7, 8, and intersecting half the distance between 1 and 2. This is shown better in the model (fig. 10), which contains more atoms, the model being oriented so that the (112) planes are in the line of vision and are those parallel to the black lines: the atoms through which the lines are drawn lie in the  $[111]$  directions.

#### (4) *Wedge Forms—Theoretical.*

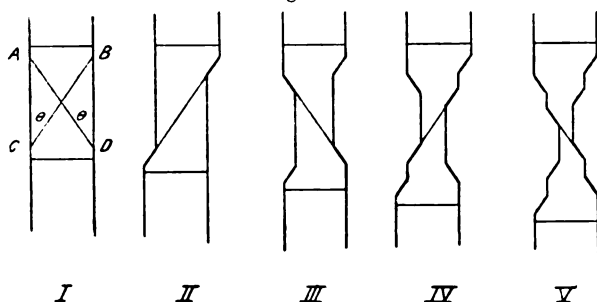
The possibility of explaining the form of the fractured crystals by slip on two sets of planes both inclined to the wire axis was briefly discussed in the previous paper. The crystal orientation with respect to the wedge forms was found to be such as to render it highly probable that the (112) planes were the planes of slip, the direction of slip being the  $[111]$  direction, and the direct determination of these in the case just discussed supports this view. It is proposed to test this supposition further by a comparison of the theoretical form assumed by a cylindrical specimen when slip occurs on two sets of planes inclined symmetrically to its axis with that actually found in the case of these wedges. Such a comparison should indicate the inclination of the planes of slip.

The manner of formation of a symmetrical wedge by means of slip on two sets of planes is best understood by considering successive stages of the process as illustrated in the series of diagrams shown in fig. 11.

Fig. 11, I, represents a section of a test-specimen which is perpendicular to two sets of slip planes parallel to AD and BC respectively, and each inclined at an angle  $\theta$  to the axis of the specimen. II-V represent successive slips on alternate conjugate planes, with the result that the crystal is

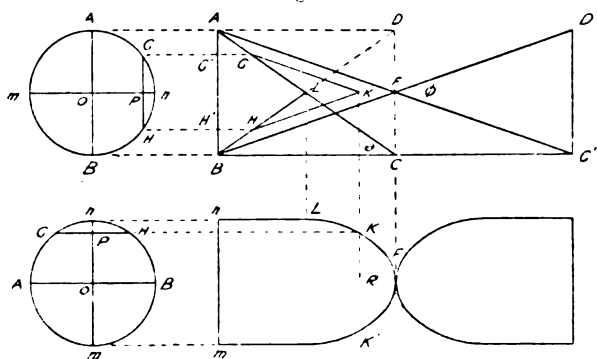
extended and at the same time reduced in diameter in the plane of the section. If the slips are small enough in comparison with the dimensions of the specimen, and if there is, on the average, as much slipping on one set of planes as on the other, it is easy to see that a completely symmetrical fracture may be produced. It should be noted that no reason is assumed for the alternation of the slipping; this will be discussed later.

Fig. 11.



It was shown in the previous paper that there is a perfectly definite relation between the resultant angle of such a symmetrical wedge and the angle  $\theta$ . This relation will hold for any section of a cylindrical specimen cut parallel to its axis and perpendicular to the planes of slip, and it should therefore be possible to determine the complete form of a fractured cylinder for any given value of  $\theta$ .

Fig. 12.



Let  $ABCD$ , fig. 12, represent a section through the axis of the cylinder of diameter  $AB$ . Let  $AC$  and  $BD$  represent the directions of two sets of slip planes in the cylinder perpendicular to the section. It was shown previously that



before fracture can occur the crystal must extend an amount  $CC'$ , such that  $CC' = BC$ . Then  $AC'$  and  $BD'$  will represent the contour of this section at the time of fracture, provided an equal amount of slipping has occurred on both sets of planes, the angle  $\phi$  being given by the relation

$$\phi = 2 \tan^{-1} \left( \frac{1}{2} \tan \theta \right) \quad . \quad . \quad . \quad (1)$$

Any other section of the cylinder at a distance  $OP$  from the axis and parallel to it will have assumed the form  $G'GKH H'$ , of which the angle  $GKH = \phi$ ; there is obviously no slipping within the portion  $G'G L H H'$ . The locus of  $K$  for all such sections is shown in the projection as the curve  $LKF$ , which is a portion of an ellipse; the outline of the two wedges is completed in the projection as shown. The two surfaces of the wedge will themselves be portions of cylinders the axes of which are inclined to the axis of the specimen.

Models have been constructed which illustrate the form assumed by a cylindrical specimen when deformed by symmetrical slip on two sets of planes. These were built up in accordance with the principle of alternate slip as illustrated in fig. 11, the angle of the slip planes with the axis of the cylinder being chosen as  $35^\circ$  to correspond to the (112) planes, and the extent of slipping regulated to give an angle of  $39^\circ$  as calculated from the theory. Photographs of these models are shown in figs. 13–16 (Pl. XVIII.). Fig. 13 shows a wedge in process of formation; figs. 14 and 15 show two views of a completed wedge taken in perpendicular directions; and fig. 16 shows the other view of the model shown in fig. 13.

#### (5) *Wedge Forms—Measurements.*

A determination of the wedge angle  $\phi$  for a large number of the fractured crystals was made by photographing the wedge forms at a magnification of 100, and measuring the mean angle between the wedge surface throughout the main portion of the wedge. The curved shoulders of the wedge where the crystals are first reduced in diameter, and the irregular tips sometimes formed at the moment of fracture through the formation of an arc or an evident distortion of the thin part of the wedge, were in all cases neglected.

The results of such measurements are given in Table I. They clearly divide themselves into two groups; Group I, long wedges with a mean angle of  $39^\circ$  and a deviation from the mean of not more than  $2^\circ$ ; Group II, short wedges with any angle from  $50^\circ$ – $60^\circ$ .

TABLE I.—Wedge Angles.

Group I.		Group II.	
Measured Angle. $\phi$		Measured Angle. $\phi$	
41°	38°	51°	52°
39	39	53	55
38	38	50	55
37	36	55	54
39	40	55	60
37	39	53	57
		52	56
Mean = 38° 24'		Mean = 54° 12'	

Substituting the mean value  $\phi = 38^\circ 24'$  in equation (1) of the last section, we get

$$\theta = 34^\circ 51',$$

which agrees well with the angle made by the (112) planes with the wire axis when the crystal orientation is symmetrical with this axis.

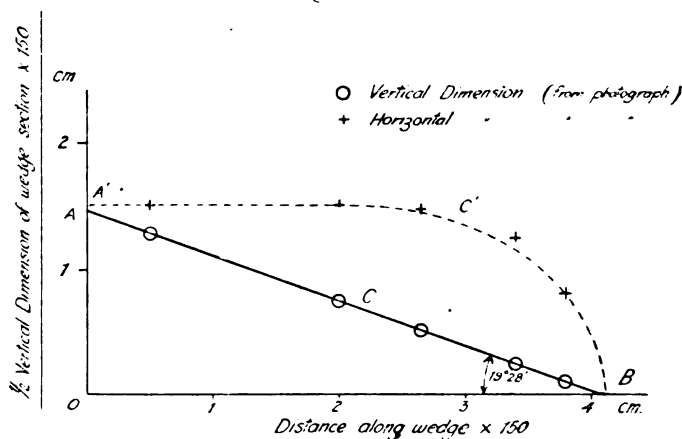
It therefore appears that this contour of the  $39^\circ$  wedges is accounted for by slip on the (112) planes, and in the [111] direction as before. The form of the other wedges having larger angles is still unexplained. This, as we shall see later, is due to unsymmetrical slip on the same set of planes and in the same direction.

It was thought desirable to check the wedge shape of the  $39^\circ$  wedges in other dimensions—in particular the theoretical contour of the wedge-edge as constructed in fig. 12, and as shown in the models. A symmetrical wedge comparatively free from end distortions and having comparatively straight wedge surfaces—such a one as shown in fig. 1 (Pl. XVI.)—was mounted in hard glass, and a series of sections made in planes perpendicular to the wire axis. Each section was photographed to show the contour, some of these being shown in the series I–VI (fig. 17, Pl. XIX.) ( $\times 150$ ).

The horizontal dimensions of these sections as measured from the photographs were compared with the theoretical

values on the same scale as shown in fig. 19. The dotted line represents the theoretical contour, and the crosses the corresponding observed dimensions in this direction. The vertical dimensions of the sections were used to locate the positions of the sections on the horizontal scale by plotting them on the line A B, O A being one-half the wire diameter as determined from the photograph VI in a vertical direction, and O B being of such a length that A B makes an angle  $\frac{1}{2}\phi = 19^\circ 28'$  with the direction of the horizontal axis. The theoretical contour was based on the wire diameter as determined from the horizontal dimension of photograph VI.

Fig. 19.



These measurements show that the wedge forms agree in other dimensions as well as wedge angle with the theoretical form, though even in this case there are evidences of some distortion, in particular section II, which is somewhat longer than the theoretical value.

#### (6) *Distortion of Crystal Planes by X-ray Analysis.*

Further evidence of distortion of these symmetrical wedge forms is shown by means of X-ray analysis. Measurements carried out in the manner described in section (3) show that the crystal planes are distorted in the direction of slip, but not in the perpendicular direction, the extent of the distortion being of the same order as that shown in the case of slip on one set of planes only. In this case the (110) planes were studied, sections being cut perpendicular to the wire

axis through the slipped portions of the wedge. Photographs such as those shown in fig. 18, I-IV (Pl. XVII.) were obtained.

Fig. 18, I, shows the effect of an undistorted (110) reflexion for the case of a symmetrical wedge deformed at  $3000^{\circ}$  K., the section being mounted so that its major axis—parallel to the wedge edge—intersected the spectrometer axis; II shows the corresponding reflexion from the section mounted so that its minor axis intersects the spectrometer axis. Similar photographs were obtained with wedges deformed at  $1000^{\circ}$  K., of which III and IV are representative. The extent of the distortion amounts to about  $10^{\circ}$  in the case of photograph II and between  $15^{\circ}$  and  $20^{\circ}$  in the case of IV. It was shown that the distortion in the case of IV was of the nature of a smooth curve throughout the section, the curvature being convex outward, viz. toward the wedge edge. This was done by covering up half of the specimen, the corresponding half of the reflected beam being in this case obliterated.

#### (7) *Microscopic Examination.*

Having established the direction of the slip planes with respect to the symmetrical long wedge forms, it appeared desirable to examine microscopically sections of these wedges cut along various crystal planes in order to co-ordinate if possible the shape of the etching pits with the orientation of the crystal. If such a co-ordination could be made, it might be expected to throw light on the nature of the distortion and the mechanism of deformation giving rise to the short wedge forms, which are still to be explained.

Sections were prepared as nearly as possible parallel to the main crystal planes within long symmetrical wedge forms. These sections were etched for 2 minutes in boiling hydrogen peroxide, and then for 45 seconds in alkaline potassium ferricyanide; they were then photographed under vertical illumination with a 3-mm. oil-immersion lens (N.A. 1.3).

The effects shown in photographs (figs. 20-23, Pl. XX.) ( $\times 250$ ) are typical of those obtained for the three main crystal planes, the (110), the (100), and the (112) planes. Figs. 20 and 21 show two views of a section cut nearly parallel to the (110) planes: such a section as would be obtained from the model shown in fig. 13 (Pl. XVIII.) when cut in a vertical plane perpendicular to the planes of slip. The photographs are mounted so that the axis of the wire is vertical in both

cases; fig. 20 is a view of the portion of the crystal through which the maximum amount of slip has taken place, and the lower part of fig. 21 is a view, near a grain boundary, of a portion of the same crystal which has not been deformed by slip. Both clearly show the same type of lamellæ with sharply-marked edges inclined at approximately  $110^\circ$  with each other, and each making the same angle with the wire axis; such markings correspond in direction with the intersection of two (112) planes with the plane of the section. It is notable that there is no evidence of any effect of slip on these markings.

Fig. 22 shows a section cut nearly parallel to a (112) plane near the tip of a symmetrical wedge: such a section as would be obtained from the model shown in figs. 14 and 15 (Pl. XVIII.) when cut parallel to one of the planes of slip. The photograph is mounted so that the wire axis lies in the vertical plane perpendicular to the plane of the section. The etching effects in this case are markedly different from those shown in figs. 20 and 21 (Pl. XX.), the heaviest markings being horizontal lines, though the absence of markings in the lower portion is particularly noticeable. These markings again correspond with the direction of the intersection of a (112) plane with the plane of the section, viz. the other slip plane inclined at  $70^\circ$  to the plane of the section.

The photograph shown in fig. 23 (Pl. XX.) was taken from a section cut nearly parallel to a (100) plane: such as would be obtained from the model (figs. 14 and 15, Pl. XVIII.) when cut parallel to its axis and parallel to the wedge edge. The etching pits appear to have no marked orientation with respect to the dimensions of the section. It should be noted that the intersection of the (112) planes with the plane of the section in this case has four-fold symmetry.

All these effects suggest that the etching reagents act more vigorously along the (112) planes than in any other direction, which is not surprising considering that this is the plane of slip, and therefore presumably of weakest bonding between atomic layers. The absence of markings in the lower part of the photograph (fig. 22, Pl. XX.) suggests that here, near the edge of the specimen, the etching reagent was able to clear off all the crystalline material along the (112) plane, which is evidently slightly inclined to the surface of the section.

On the strength of these results the examination was extended to various sections made from wedge forms, with the object of obtaining any information which might lead to a better understanding of the mechanism of their formation.

Photographs figs. 24-30 (Pls. XXI. & XXII.) were some of the most interesting of those obtained. These were taken at a magnification of 750 with the same lens as before.

Fig. 24 shows the central portion of the crystal shown in fig. 20 (Pl. XX.). It brings out the markings more clearly, and serves as a comparison for the photograph (fig. 25) showing the tip of the short wedge shown in fig. 6 (Pl. XVI.) taken at low magnification; these photographs are mounted so that the wire axis is vertical in both cases. The markings shown in the photograph fig. 25 clearly suggest that the final fracture of this crystal has taken place by slip along a (112) plane from left to right, and it is to be noted that the angle made by this plane with the axis of the wire is about  $40^\circ$ .

Fig. 26 shows the tip of another such short-wedge form, but this time from a wire fractured at  $1000^\circ$  K. and under a load of 14 kg./mm.<sup>2</sup> The photograph is again mounted so that the wire axis is vertical. The markings appear in every way the same as those shown in fig. 25, though there is evidence of greater distortion of the crystal. Again the final slip appears to have taken place along a (112) plane, the inclination of this plane to the direction of stress being, as before, about  $40^\circ$ . These two forms are indeed typical of all the short wedges examined, and, as we shall see, give the clue to a possible explanation of their formation.

Fig. 27 shows the tip of a very irregular wedge form, the photograph being mounted so that the wire axis is vertical. This form is such as to leave no doubt that slip has occurred in the direction of the etch markings. The photograph is of special interest because both the  $70^\circ$  angles and the  $110^\circ$  angles made by the (112) planes are to be seen. Marked curvatures of the planes are evident however, the planes having suffered a change of orientation of about  $20^\circ$  between successive slips in the last few large slips shown: such a distortion, though large, is not inconsistent with the results of X-ray analysis already given.

Fig. 28 (Pl. XXII.) shows a section of a wedge almost parallel to the (110) plane but perpendicular to the wire axis: such a section as that shown in fig. 17, III (Pl. XIX.), and similar to those used for X-ray analysis described in (6). The photograph is mounted so that the major axis is vertical. The markings are clearly similar to those obtained from other (110) sections, but—in agreement with the results of X-ray analysis—there is distinct evidence of distortion symmetrical with the major axis of the specimen.

The photographs figs. 29 & 30 were obtained from the

two sections described in (6), of which the distortions were compared in fig. 18, I-IV (Pl. XVII.). The  $70^\circ$  markings are predominant in these sections, their asymmetry about the vertical axis, particularly in fig. 30, being most marked.

The photograph fig. 31 (Pl. XXII.) is a view of one end of the section, described in (3), cut along the plane of slip; it is mounted so that the major axis of the section corresponding to the direction of slip is nearly vertical. The markings clearly resemble those shown in fig. 22 (Pl. XX.), and the evidence of distortion, especially near the bottom of the section, is clearly seen; further, this distortion appears to be symmetrical about the horizontal direction in agreement with the results of X-ray analysis.

#### (8) *Effect of Orientation on Mode of Deformation.*

The sharpness of the markings indicating the direction of the slip planes in the etched sections of these crystals suggests the possibility of determining by this means the crystal orientation in the various crystal forms produced by deformation.

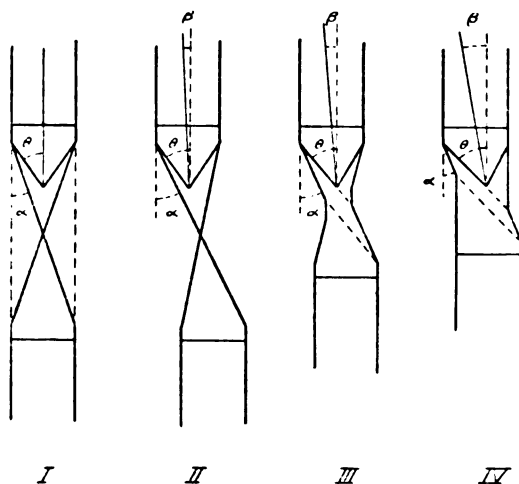
A study of the effect of orientation on the shape of the deformed crystals, in particular those which have not fractured, should yield information concerning the relative tendency to slip under conditions of stress which are strictly comparable. Since these crystals were taken from test-wires which were actually fractured, the load, time of application of the load, and temperature were the same as were required for the fracture of the weakest crystal.

Sections were cut as nearly as possible parallel to the (110) planes perpendicular to the planes of slip in the case of a variety of typical crystal forms. These were prepared in the usual way and were photographed at two magnifications, one at 70 and the other at 250. The direction of the wire axis in the case of the latter was determined by comparison with the direction of the wire axis as shown by the former. Measurements were made on the high magnification photographs by drawing lines parallel to the etch markings and measuring the angles made by these lines with the direction of the wire axis; a mean of at least 10 readings was taken in the case of the best photographs. Four of these photographs are shown in figs. 32-35 (Pl. XXIII.), the photographs being mounted so that the wire axis is vertical in each case. Fig. 32 shows the somewhat drawn-out tip of a symmetrical long wedge; fig. 33, an unsymmetrical wedge; fig. 34, a

portion of a crystal which has slipped largely, but not entirely, on one set of planes; fig. 35, one which has slipped almost entirely on one set of planes.

The results of the measurements clearly show that the orientation of the crystal with respect to the wire axis determines the form assumed by the crystal. The facts are represented diagrammatically in fig. 36. If we consider the line bisecting the angle between the two sets of slip planes as representing the inclination  $\beta$  of the crystal to the wire axis, then, as  $\beta$  increases from zero, the crystal

Fig. 36.

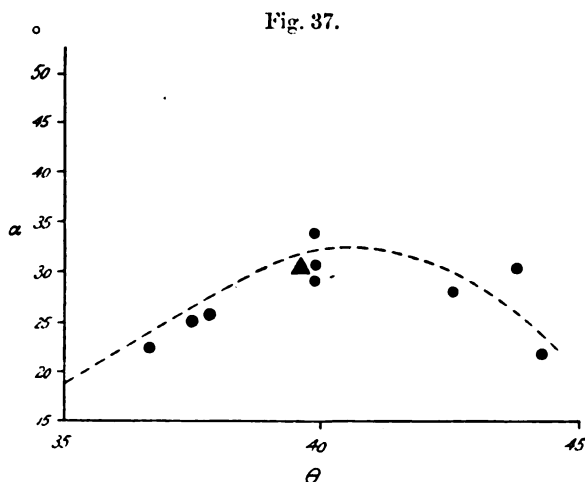


forms change from the symmetrical form shown in I to the asymmetrical forms shown in II, III and IV, a further increase resulting presumably in no deformation whatever. Such asymmetrical forms can only be produced by differences in the extent of slipping on the two sets of planes and the form shown in III indicates that the extent of slipping on the more oblique set of planes is greater than in any of the other forms since the obliquity of the surface here reaches a maximum.

The most favourable angle for slip on any one set of planes may, therefore, be determined by plotting the measured values of  $\alpha$ —the angle between the more oblique crystal surface and the wire axis—against the corresponding values of  $\theta$ —the angle made by the slip planes with the wire axis.



The results are shown in fig. 37; the triangle represents the relation between  $\alpha$  as measured from the photograph fig. 7 (Pl. XVII.) and the mean values of  $\theta$  as determined by X-ray analysis. Clearly  $\alpha$  rises to a maximum, the corresponding value of  $\theta$  being about  $40^\circ$ .



Though no great accuracy can be expected from such measurements, they are considered as sufficiently representative of the facts to warrant the general conclusion that the tendency for slip to occur on any one set of planes is greater the nearer the inclination of the set of planes with respect to the wire axis approaches an angle of about  $40^\circ$ .

#### (9) *The Mechanism of Wedge Formation.*

The effect of crystal orientation on the tendency to slip, coupled with the facts of crystal distortion, suggest the explanation of the formation of the crystal wedges, in particular the large angle short wedges which have not yet been explained.

The photographs figs. 25 & 26 (Pl. XXI.) clearly indicate that fracture occurred by a final slip practically on one plane inclined at an angle of about  $40^\circ$  to the wire axis. On the other hand, the inclination of the other surface forming the wedge angle shows that slip must have occurred previously on the conjugate set of planes, the inclination of which must have approached  $40^\circ$  at the time when slip took place. The suggested explanation is that the short wedges are produced

in crystals which are slightly inclined to the wire axis; that, in consequence of this, slip in the beginning occurs mainly on one set of planes in the manner represented in diagram III (fig. 36); that the asymmetry of the form thus produced results in the re-orientation of the crystal in the region of reduced cross-sectional area, until the inclination of the conjugate planes is sufficiently favourable to result in slip, the most favourable angle being about  $40^\circ$ . This accounts for the large angle of these wedges, the total angle being  $40^\circ$  plus the angle produced by the succession of slips on the conjugate planes.

A similar process is no doubt involved in the formation of the long  $39^\circ$  wedges, the forms of which have been explained by assuming alternate slipping on two sets of conjugate planes symmetrically inclined to the wire axis in regions of progressively reduced cross-sectional area as represented in the series of diagrams shown in fig. 11. In the discussion of these wedge forms (4), however, no reason was given for the alternation of the slipping and the maintenance of the crystal stability during the process of deformation. The process of crystal distortion favouring slip on the alternate planes affords a possible explanation, especially since the amount of distortion required to change the balance in favour of slip on the conjugate planes need not be large. Fig. 27 (Pl. XXI.) shows clearly that such an action does actually occur in the case of this somewhat irregular long wedge form. In the photographs (fig. 24, Pl. XXI. and fig. 32, Pl. XXIII.) no evidence of the distortion appears, but it is to be expected that if the extent of slipping on each set of planes is small, the distortion would not be large, and, moreover, each successive distortion would tend to correct the previous one. It has been shown that the crystal wedges are distorted, the  $\{110\}$  planes—perpendicular to the wire axis—being convex toward the wedge edge. This can be accounted for by the effect of distortion due to the successive slips, if we assume that the slip planes tend to become distorted near their edges, the distortion reaching a maximum in the region where the overlapping is greatest. It would be expected that these planes would be pulled more nearly into the line of stress owing to the disturbance in the balance of forces due to overlapping. Under these conditions the crystal may be distorted momentarily, favouring slip in the conjugate planes until the process is reversed.

It should be pointed out, however, that such a crystal re-orientation is not necessary to explain the formation of these wedges, it being only necessary to assume that slipping,

once started on any plane, automatically stops, and that the next slip occurs in a new region of the crystal. Since slipping on one set of planes tends to reduce the volume of the crystal in which slips may occur on like planes of equal area, whereas it tends to increase the volume for conjugate planes of equal area (see diagrams, fig. 11), it follows that the probability of slip occurring in any volume of the crystal tends to favour the conjugate planes. The tendency for slip to be automatically limited finds a ready explanation in the distortion of the crystal planes in the direction of slip, especially near the edges, where there is a disturbance in the balance of forces due to overlapping; such a distortion was shown to be produced in the zone of slip in the case of the crystal in fig. 7 (Pl. XVII.), which was deformed by slipping on one set of planes.

(10) *Special Case of Slip on (100) Planes.*

In the course of the investigation on the strength of these crystals, a freak case of fracture was observed which is of some significance. Figs. 38 and 39 (Pl. XXIV.) show two views of this fracture taken in perpendicular directions. They show that two wedge forms are produced which are inclined to each other at  $90^\circ$ . One of these wedge forms is very much like the long  $39^\circ$  wedge: such a wedge is shown in fig. 40 (Pl. XXIV.) for the sake of comparison. The other is of a much larger angle, measuring over  $60^\circ$ . A series of etched sections cut perpendicular to the wire axis and mounted with the proper relative orientation is shown in fig. 41, I-IV (Pl. XXIV.). They clearly show that the double wedge was formed from the same crystal, and that the cause of this formation lay in the groove, produced by a split in the wire in which the crystal was grown. The inclination of this groove was such as to prevent slip in the normal way. It was shown by X-ray analysis that the crystal section as shown in IV was nearly parallel to the (110) planes. This makes it practically certain that the narrow wedge was due to slip on (112) planes, and that the other wedge was produced by slip along (100) planes. The theoretical angle for this latter wedge would be  $54^\circ$ , but the actual angle is no doubt due, as in the case of short wedges, to asymmetrical slip accompanied by distortion. It may be observed that the force required to produce this fracture was larger than that required for a normal fracture, the breaking stress being  $16 \text{ kg./mm.}^2$  at  $1200^\circ \text{ K.}$  as compared with  $12 \text{ kg./mm.}^2$  for a normal wire at the same temperature.

(11) *Discussion of Results.*

It has now been established that all of the deformed crystals studied, in particular the fractured crystal wedges, can be accounted for by a process of slip on the (112) planes and in the [111] direction, with the single exception of the specially constrained crystal, in which slip also occurred on the (100) planes and in the [100] direction. All such deformed crystals showed distortions which affected the inclination of the crystal planes in the direction of slip, but which produced no marked change in the atomic spacings.

Further, it has been shown that the most favourable crystal orientation for extension and fracture is such that two sets of 112 planes are inclined at  $35^\circ$  to the wire axis, whereas the most favourable orientation for slip on one set of planes is such that the planes make an angle of about  $40^\circ$  with the wire axis.

The direction of slip, the [111] direction (viz. along the cube diagonal), is that of the densest packing of atoms for this type of crystal lattice (viz. the body-centred), the distance between the atoms along this line being smaller than along any other line of atoms in the crystal. The result is therefore in agreement with that obtaining in the case of the deformation of single crystals of other metals involving different lattice types, viz. zinc, tin, bismuth, and aluminium, as pointed out by Polanyi\*. The one case in which slip occurred in the [100] direction (viz. along the cube edge) demonstrates the fact that slip can occur along other lines of atoms as well; further, it is to be noted that this direction is next in order to the [111] in the density of atoms. The nature of the constraints induced by the peculiar form of this crystal and the extra stress required to produce the deformation suggest that, under suitable conditions, a crystal could be made to slip in still other directions, and that such is in fact the case when a crystal is deformed as part of an aggregate.

The extent of the distortion produced by the deformation of these crystals is such that they can no longer be considered as "single crystals" in the strict sense. It follows both from the X-ray measurements and from the photographs that distortions of the crystal occur which would involve an atomic displacement of at least 10 per cent. in some cases, whereas no such displacement was observed: a displacement of 10 per cent. could easily be detected. It would appear

\* Polanyi, *Zeit. f. Phys.* xvii. pp. 42-53 (1923).

that the crystal must be considered as made up of small, more perfect crystals with similar but not the same orientations. The mechanism of deformation, which satisfactorily accounts for the crystal forms, suggests that although the major portion of the slipping occurred before an appreciable amount of distortion took place,—with the exception of the slips near the point of fracture,—it is because of this distortion that slip is limited in extent along any one plane. If we take the view that slipping is merely a handing-on of atomic bonds, it is easy to see why a small curvature of the planes involving gaps or local changes in bonding in the chain of atoms would increase the resistance to slip.

The most favourable crystal orientation for extension and fracture is that which has been found to occur most frequently in worked crystal aggregates of tungsten, in particular drawn tungsten wire and rolled tungsten foils \*. In both cases one set of (110) planes tends to set itself perpendicular to the direction of stress, and in the case of rolled foils the (100) crystal faces tend to lie in the plane of rolling. In the light of our experiments the reason for this becomes quite clear, in that extension can take place mainly by slip on the (112) planes inclined at  $35^\circ$  to the plane of rolling, and at the same time increase of width and some extension can take place by slip on the (100) planes. The fact that the tendency for slip to occur increases above  $35^\circ$  has been shown to account for the stability of crystals during deformation by extension when in this favoured crystal orientation. This is in agreement with the hypothesis put forward by Polanyi † to account for the stability of the favoured crystal orientations in worked metals. The fact that the most favourable angle for slip on one set of planes is about  $40^\circ$  and not  $45^\circ$  is worthy of note. Since the theoretical orientation for maximum shearing stress is  $45^\circ$ , the result would appear to indicate that the perpendicular component of stress is effective in producing slip in this case, but further experiments will be necessary in order to settle this point.

These experimental results demonstrating that the mechanism of fracture is in all cases the same are of importance in connexion with the interpretation of the strength measurements described in the previous paper. Discontinuities were found to occur in load-temperature curves at definite temperatures which were co-ordinated with variations in other

{ \* Polanyi, *loc. cit.*

† Polanyi, *loc. cit.*

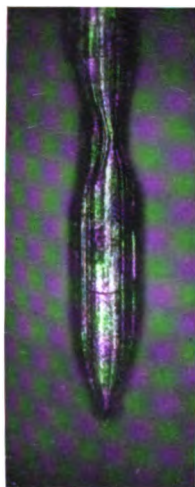


FIG. 1.

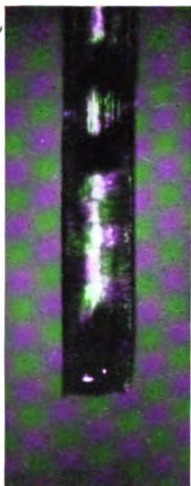


FIG. 2.

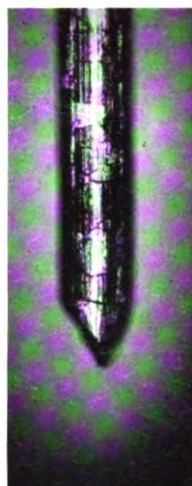


FIG. 3.

Figs. 1, 2, 3. Exterior view of fractured wires showing deformed crystals ( $\times 50$ ).

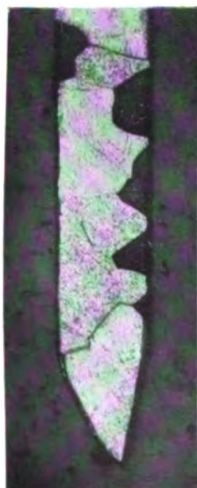


FIG. 4.



FIG. 5.



FIG. 6.

Figs. 4, 5, 6. Etched sections of fractured wires showing deformed crystals ( $\times 70$ ).



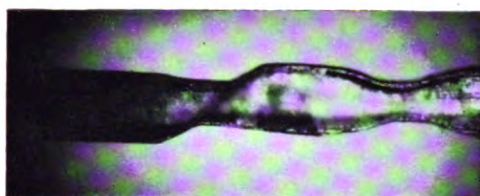


FIG. 7.

Fig. 7. Deformed crystal (left) which has slipped almost entirely on one set of planes ( $\times 50$ ).

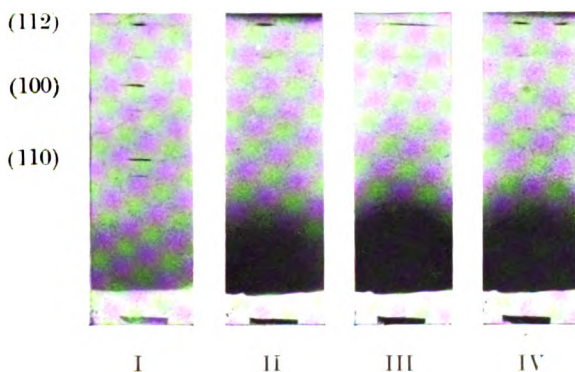


FIG. 8.

Fig. 8. X-ray photographs of (112) reflexions from planes of slip shown in crystal fig. 7 showing distortion of these planes.

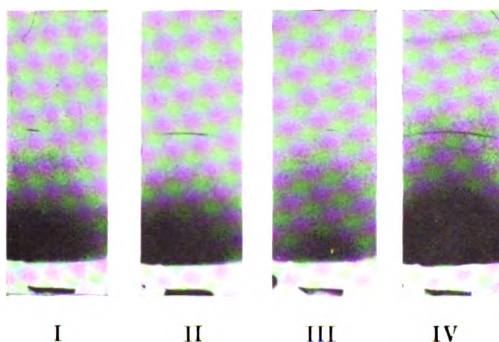


FIG. 18.

Fig. 18. X-ray photographs of (110) reflexions from sections of wedges perpendicular to wire axis showing distortion of these planes.





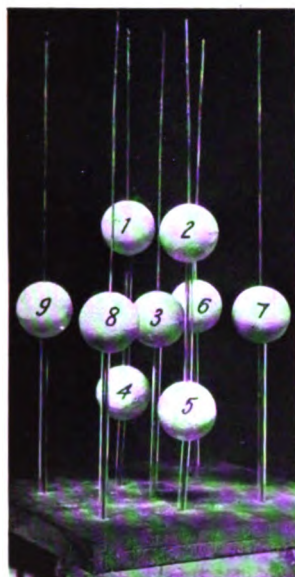


FIG. 9.

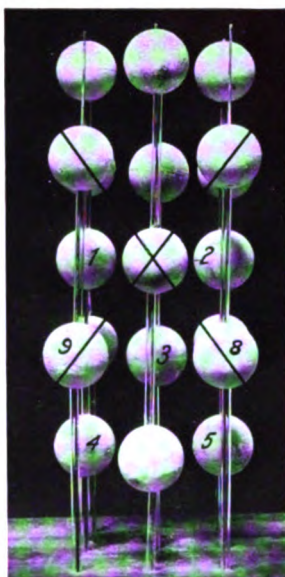


FIG. 10.

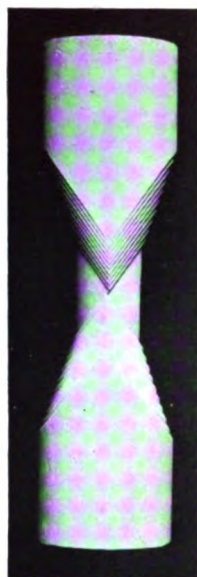


FIG. 13.

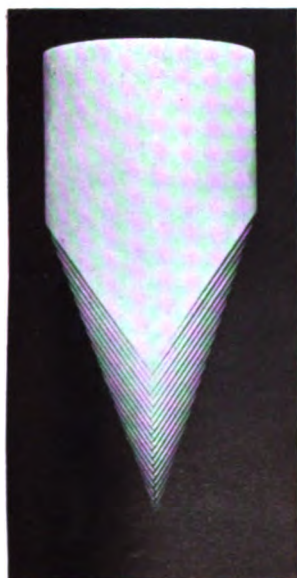


FIG. 14.



FIG. 15.



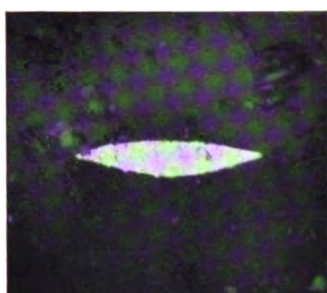
FIG. 16.

Figs. 13, 14, 15, 16. Models showing forms assumed by a cylinder when deformed by slip on two sets of planes symmetrically inclined to its axis.





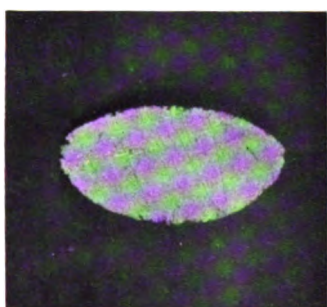
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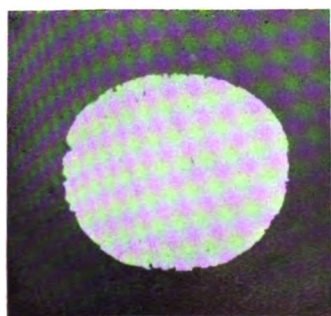
II



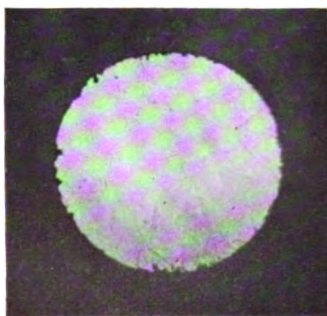
III



IV



V



VI

FIG. 17.

Fig. 17, I-VI. A series of sections cut from a symmetrical wedge perpendicular to wire axis ( $\times 150$ ).





FIG. 20.

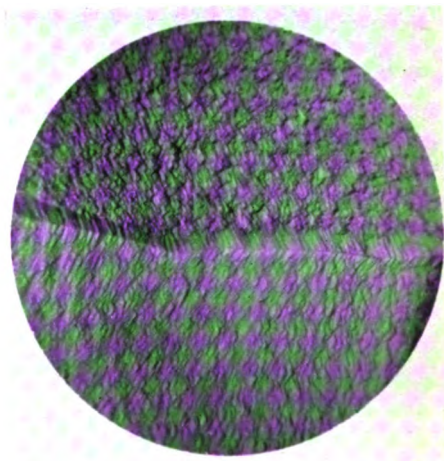


FIG. 21.

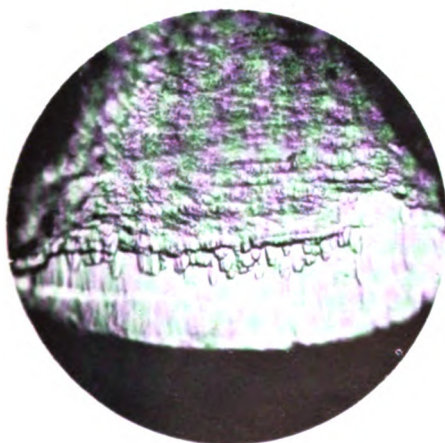


FIG. 22.

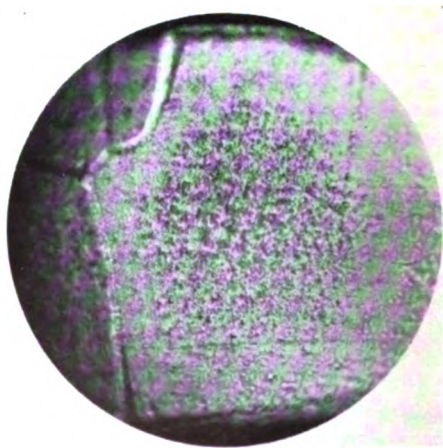


FIG. 23.

Figs. 20, 21, 22, 23. Etched sections from wedge forms cut parallel to (110), (112), and (100) planes showing characteristic etching effects ( $\times 250$ ).





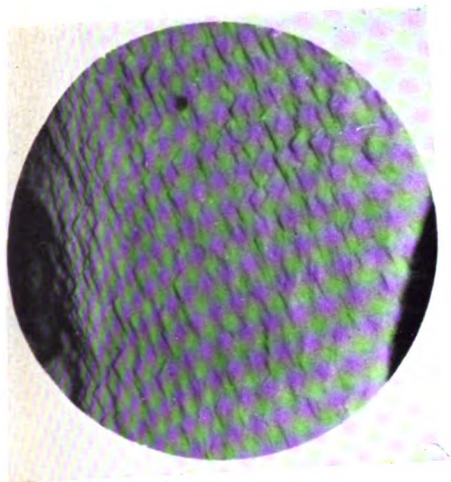


FIG. 24.

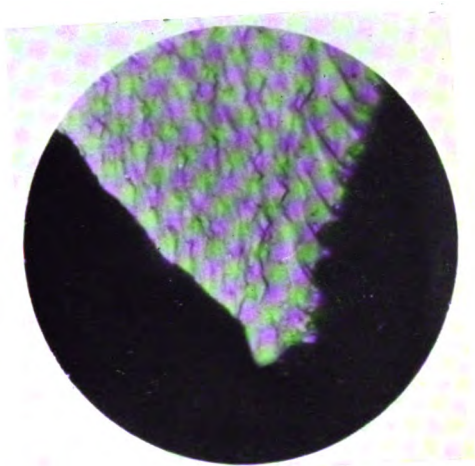


FIG. 25.

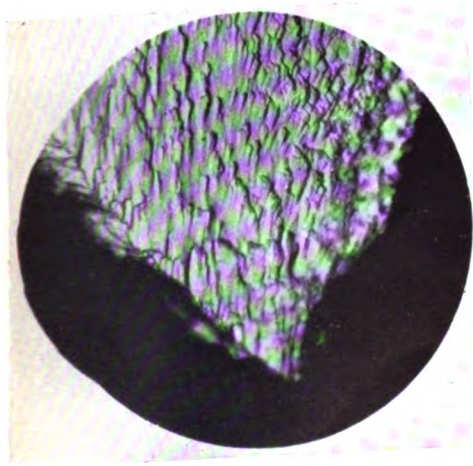


FIG. 26.

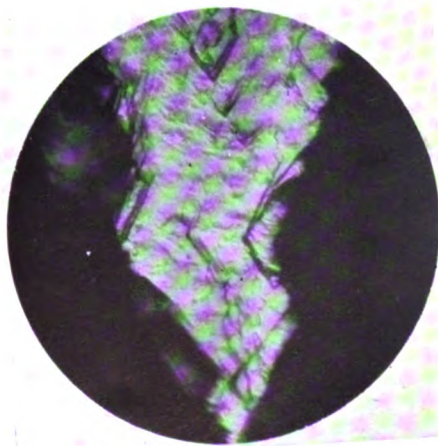


FIG. 27.

Figs. 24, 25, 26, 27. Etched sections from wedge forms perpendicular to planes of slip showing distortions of slip planes ( $\times 750$ ).





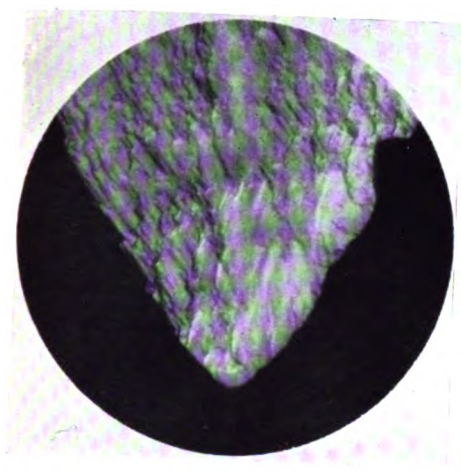


FIG. 28.

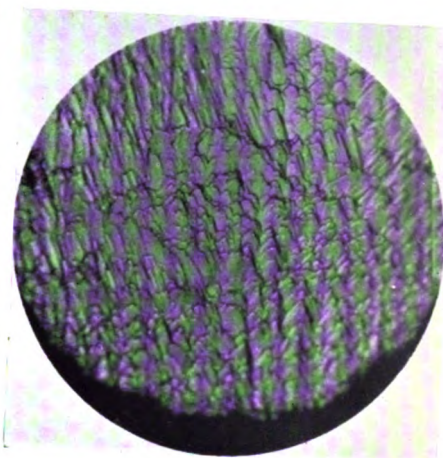


FIG. 29.

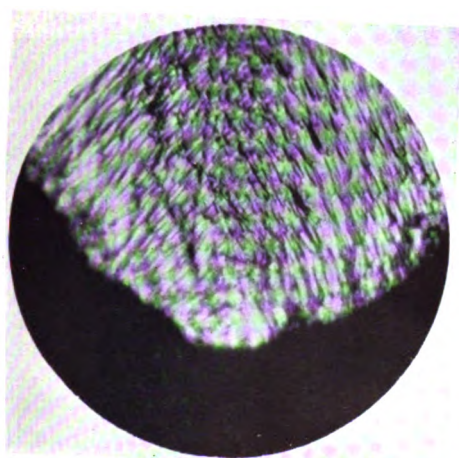


FIG. 30.

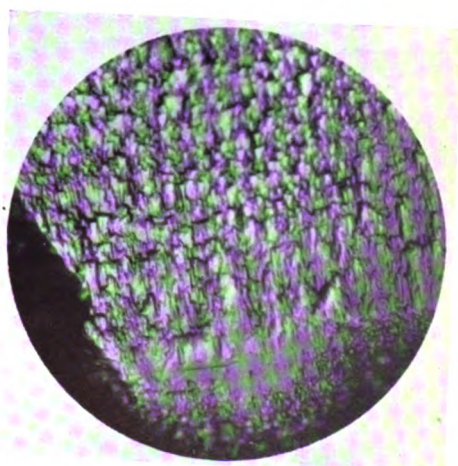


FIG. 31.

Figs. 28, 29, 30. Etched sections from wedge forms perpendicular to wire axis showing distortions.  
Fig. 31. Section along slip plane showing distortion ( $\times 750$ ).



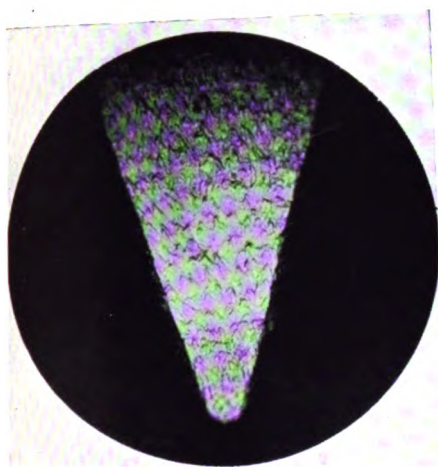


FIG. 32.

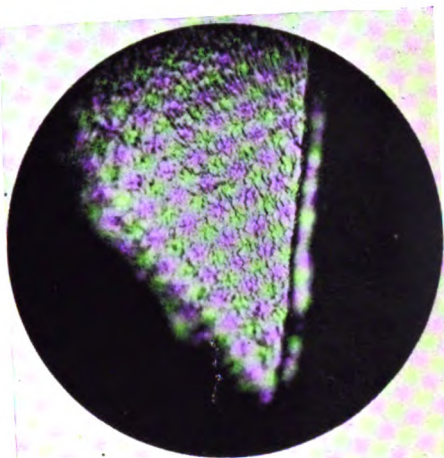


FIG. 33.

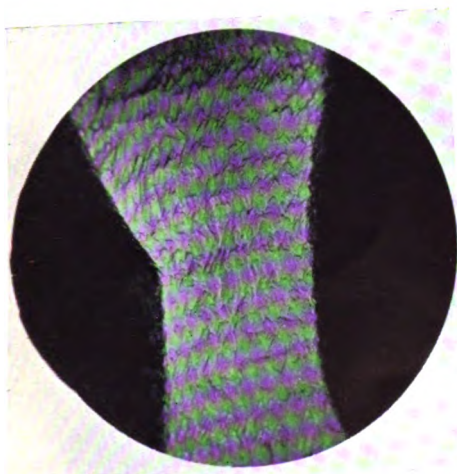


FIG. 34.

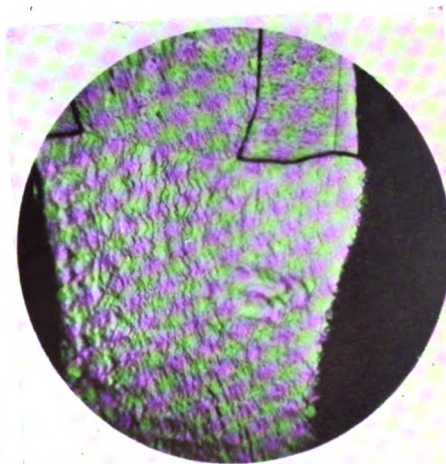


FIG. 35.

Figs. 32, 33, 34, 35. Etched sections from typical crystal forms showing crystal orientation ( $\times 250$ ).



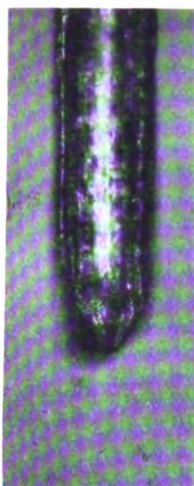


FIG. 38.

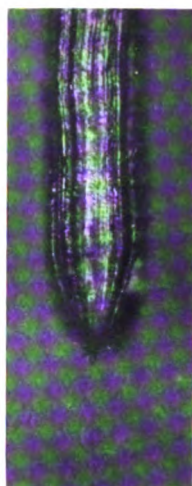


FIG. 39.

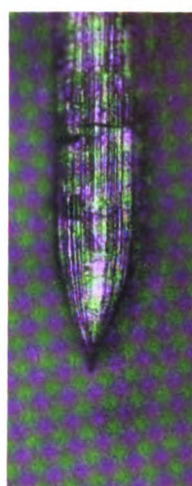
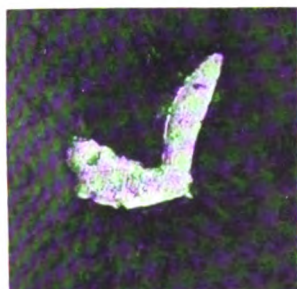
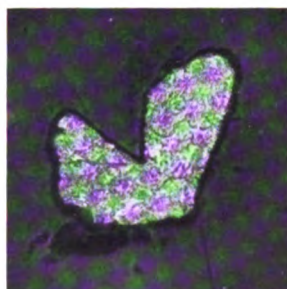


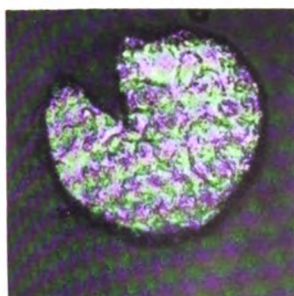
FIG. 40.



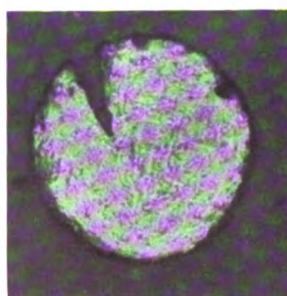
I



II



III



IV

FIG. 41.

Figs. 38, 39. An abnormal fracture showing two wedge forms inclined at right angles ( $\times 70$ ).

Fig. 40. A normal fracture showing wedge angle ( $\times 70$ ).

Fig. 41. A series of etched sections cut from abnormal wedge fracture showing that double wedge form was produced from same crystal.





physical properties, leading to the view that a new type of transformation was involved. The character of the curves in the neighbourhood of one of these discontinuities varied somewhat, depending apparently on the previous history of the wires in which the fractured crystals were grown. The present experiments establish that the measured forces have to do with the overcoming of atomic bonds of a perfectly definite type, and lend support to the view that this is merely a handing-on of atomic bonds—the atoms moving on to their new positions on the lattice; but they also show that the process is complicated by distortions which may very materially alter the strength measurements. It may well be that very slight differences in the perfection of the crystal before deformation will produce marked effect on the ability of the crystal to distort.

Research Laboratory of the  
General Electric Company,  
August 1st, 1924.

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LXXX. *The Radioactivity of Basalts and other Rocks.*

*By J. H. J. POOLE, Sc.D., and J. JOLY, F.R.S. \**

IT has been shown in several recent papers that the geological history of the earth's crust depends very largely on the radioactivity of the sub-crustal magma. It is accordingly important to determine, as far as possible, what the absolute radioactive content of the magma actually is, since the time-interval between successive geological revolutions will depend on its value, and may be roughly estimated when the value is known. It is obviously impossible to deal with the problem directly, but, fortunately, it is now fairly well established that the magma is of a basic character, with a lower layer of possibly ultra-basic nature; and thus by determining the radioactivity of the basic and ultra-basic surface materials of the crust, we should be able to arrive at a very fair estimate of the radium content of the parent magma.

In order to measure the total radioactivity of a rock, it is necessary to determine both its radium and thorium contents. The effect due to the actinium series is so small that it is negligible in comparison with the probable errors in determining the small amounts of radium and thorium involved.

\* Communicated by the Authors.



The actinium content of a rock has never, as far as we are aware, been directly determined, but can, of course, be approximately calculated from its radium content. In all the results given in this paper the radium content has been measured by the electric furnace method, and the thorium content by the solution method. To obtain as fair a mean value for the radioactivity of the underlying magma as possible, all available specimens from different localities have been dealt with. It may be remarked that the results show that this precaution is necessary, as the various basaltic outflows may differ appreciably in radioactivity. Thus, while the Hebridean outflow is rather below the average, the Coloradian is distinctly above it, and if we restricted our experiments to either we should obtain deceptive results.

Turning to the actual technique of the experiments, the method of procedure in determining the radium content of a rock by the electric furnace has been fully described in previous papers\*. The method briefly consists in fusing about 8 g. of the powdered rock with 24 g. of mixed alkali carbonates in an electric tube furnace capable of giving a temperature of about  $1100^{\circ}$  C. The emanation which is liberated from the rock powder by the resulting chemical decomposition is transferred to an electroscope, where its effect on the rate of leak is measured. The effect of a known amount of radium emanation on the electroscope being previously determined, we can then calculate the amount of radium in the rock powder. For further details of the process the original papers may be consulted. The chief sources of uncertainty in the results may be summarized as follows. They are:—

- (1) Exact value of constant of electroscope.
- (2) Radioactive contamination of rock powder.
- (3) Radioactive contamination of carbonates etc.
- (4) Adsorption of radium emanation by soda-lime used for removal of  $\text{CO}_2$ .
- (5) Incomplete washout of furnace.
- (6) Presence of slight traces of water-vapour in the electroscope.
- (7) Irregularity in the natural leak of the electroscope.

We will now deal with the methods adopted for reducing or eliminating these various sources of error.

Considering first the determination of the constant of the

\* Joly, *Phil. Mag.* July 1911 and Oct. 1912.

electroscope, a new and improved method has been devised, 10 m.g. of uraninite of known uranium content were added to about 30 g. of radium-free borax glass, and the mixture fused, the melt being well stirred to ensure perfect mixing. The total weight of the melt was carefully ascertained, and hence we could calculate its uranium content per gramme. The melt was then ground up, sifted from finest powder, and stored in a glass tube for future use. When it was desired to standardize the electroscope, a suitable quantity of this powder was added to a rock powder, whose effect on the electroscope had already been determined, and the effect of the resulting mixture determined in the ordinary way. The net increase in the rate of leak of the electroscope over the rate of leak due to the rock powder alone will then be due to the radium content of the amount of the standardizing mixture used; and as this quantity is known, we can accordingly calculate what amount of radium corresponds to a gain in leak of one scale-division per hour. The advantages of this method are twofold—first, we can obtain very small quantities of uraninite without any very delicate weighings; and, secondly, the conditions under which the standardization experiment are conducted are practically identical with every other rock experiment. The object of having the rock present is that by its decomposition it may supply  $\text{CO}_2$  to carry off the emanation from the melt. The amount of standardizing mixture used was so chosen that its radium content might be as nearly as possible the same as that of the class of rock which was being dealt with at the time. The constant of the electroscope was frequently determined by this method. Its value was found to vary from about 0.65 to about  $0.8 \times 10^{-12}$  g. of radium per scale-division per hour. This alteration in the value of the constant is probably to be attributed to differences in the size of grain of the soda-lime used in the absorption tubes, which would probably lead to different amounts of emanation being stopped by the tube. This point will be referred to again later. For some of the earlier experiments, in which the constant was determined by adding a weighed small quantity of uraninite directly to the rock powder, a rather lower value was obtained (0.5); but as the results, given by this constant, were subsequently confirmed when working with the higher constant, they have been included in the published values.

As far as the second error due to contamination of the rock powder is concerned, we may probably consider it as

eliminated. The rock was ground up immediately before an experiment in a room in which no radium had ever been handled; and none of the various operators ever at any time during the course of the experiments came in contact with any possible source of contamination. The constancy of the results obtained is probably sufficient proof that no contamination could be taking place, as, if it had occurred, it would most certainly have led to much larger variations in the results from day to day. The possible contamination or, rather, radioactive impurity of the alkali carbonates is, however, a much more serious question, partaking as it does of the nature of a constant error, which will not be evident from mere inspection of the results. Several tests of the radium content of the carbonates were made, and although many of them gave null results, yet some seemed to indicate that they might contain small sporadic quantities of radium, which would vitiate the values obtained for the rock specimens. On this account a new method of dealing with the carbonates was adopted. Immediately before an experiment, the 24 g. of alkali carbonates were dissolved in water, boiled, and then evaporated to dryness in an evaporating basin. The carbonates are then immediately mixed with the rock powder in the usual way, placed in the platinum boat, and the experiment proceeded with in the ordinary fashion. The effect of this procedure is that any radium emanation the carbonates may contain is driven off in the preliminary boiling, and hence the radium content, if any, of the carbonates cannot affect the final result. In some cases, as has been described in previous papers, it is necessary to use small quantities of boracic acid to encourage a free evolution of  $\text{CO}_2$ , and this material, when used, is de-emanated in a similar fashion. This plan of de-emanating the chemicals was only adopted fairly late on in the series of experiments, and accordingly it was thought advisable to check some of the earlier results. The results obtained by the two different methods are shown in separate columns in the lists published. It will be seen that in most cases the agreement between the two is quite good, showing that on the average the radioactive impurity of the chemicals must be small.

The possibility of the soda-lime tube adsorbing some of the radium emanation is a troublesome one, and has not yet been overcome. The obvious way of dealing with the matter is to eliminate the soda-lime tube, and pass all the  $\text{CO}_2$  directly into the electroscope. Unfortunately this would involve using too large an electroscope if we employ the usual 8 g. of rock powder; and if we reduce this amount much, we shall

not be able to measure the increase in rate of leak with any accuracy. Any other plan of preventing the  $\text{CO}_2$  from reaching the electroscope, such as freezing it out, would also labour under the same suspicion that it prevented some of the emanation also from reaching the electroscope. It is hoped in future, however, to make the electrical measurements more sensitive by using a Lindemann Electrometer, and hence to be able to use a smaller quantity of rock and deal with the total volume of  $\text{CO}_2$  evolved. Meanwhile there is, of course, good reason to expect that the effect of the adsorption, if any, will be practically eliminated by the comparison method adopted for standardizing the electroscope.

As regards the possibility of the furnace not being completely washed out of emanation, this point had been tested previously by filling a second electroscope through the furnace immediately after the conclusion of an experiment. The second electroscope showed practically no increase in leak, showing that no emanation had been left in the furnace system. This test does not, of course, prove that the soda-lime had not adsorbed the emanation to a certain extent, as the latter would probably not be liberated by simply drawing air through the soda-lime tube. The effect of traces of moisture getting into the electroscope is troublesome, and on this account good drying tubes must be used, and the electroscope filled not too quickly. The danger is that there is usually a large amount of water evolved during the decomposition of the rock; and if even a small trace of this gets into the electroscope, it will give a spuriously high result if the latter is read immediately. However, we can fairly easily discriminate between this water-vapour effect and the true radioactive effect by rating the electroscope immediately after the transference and also three hours later. If the effect is truly radioactive, the net gain in leak should show about a 30-per-cent. increase at the end of three hours, but if it is partially due to water-vapour, there may be no increase, or even possibly a slight decrease at the end of the three hours. Thus experiments in which the correct increase is not shown have been excluded. It is, however, quite easy to avoid this error by renewing the drying materials fairly frequently.

The irregularities sometimes observed in the natural leak of the electroscope were found to be due to two causes. One is the effect of light on the sulphur insulation of the gold-leaf system, which is quite large, and the other the accumulation of slight traces of radioactive products in the atmosphere of the laboratory unless a good circulation of air is maintained. The result is that the electroscope must be kept

in the dark as much as possible and the room kept well ventilated. When these precautions were observed, the natural rate of leak remained quite sufficiently constant. It was found also that under these conditions there was no advantage in filling the electroscope with air drawn in directly from outside the building.

Turning next to the consideration of the thorium content, this was determined, as has already been mentioned, by the solution method. The details of this method have already been published in the 'Philosophical Magazine' for May 1909. The solutions used were prepared from the melts obtained from the experiments with the electric furnace. These melts were carefully ground up and then treated with pure water. After standing for at least 6 hours, the resulting mixture was filtered. The filtrate is discarded, as it contains no thorium, and the residue dissolved in dilute pure HCl and then made up to a convenient bulk with water. It is usually possible to obtain a perfectly limpid rock solution by this method; but if too concentrated HCl is used, or if the decomposition is not complete owing to the furnace not having reached a sufficiently high temperature, we are apt to get a cloudy solution, owing to the presence of gelatinous silica. Previous experiments have, however, shown that this cloudiness has no very marked effect on the value obtained for the thorium content of the solution.

The amount of thorium in the solution is determined by boiling it in a constant current of air, which is subsequently passed through a reflux condenser and set of drying tubes into an electroscope whose rate of leak any thorium emanation liberated from the solution will affect. In order to eliminate the radium emanation, the solution is previously boiled for about twenty minutes in an open flask. The electroscope is standardized in the ordinary way by using a solution containing a known amount of thorium. It is obvious that the constant of the electroscope will depend on the velocity of the air-current, and it is easy to show that there is a certain value of this velocity which will give the lowest value of the constant. Thus, if we let  $N_0$ =number of thorium emanation atoms escaping from the solution per second,  $V$ =velocity of air-stream in c.c. per sec.,  $a$ =volume of condenser etc.,  $b$ =volume of condenser and electroscope, and  $\lambda$ =the radioactive constant for thorium, we see that, when a steady state has been attained,  $N$ , the number of atoms breaking up per second in the electroscope, will be equal to

$$N_0 \left[ e^{-\frac{\lambda a}{V}} - e^{-\frac{\lambda b}{V}} \right].$$

This quantity will be a maximum when

$$e^{-\frac{\lambda a}{V}} \cdot \frac{\lambda a}{V^2} - e^{-\frac{\lambda b}{V}} \frac{\lambda b}{V^2} = 0$$

or

$$ae^{-\frac{\lambda a}{V}} = be^{-\frac{\lambda b}{V}},$$

which gives

$$V = \frac{\lambda(b-a)}{\log b - \log a}.$$

The value for the volume of the condenser system which has to be inserted in this expression is not the actual total volume, but only that fraction of it which is not occupied by water-vapour. As this fraction is not known, we can only calculate approximately what the best value of the air-current should be. Putting in, however,  $a = 50$  c.c., which from the dimensions of the actual apparatus would appear to be a fairly reasonable value,  $V$  comes out to be about 3 c.c. per sec. In practice the best value of  $V$  was determined by trial, and about 4 c.c. per sec. was found to give the best results, so the agreement with the theoretical value is satisfactory. The method used of obtaining a steady current of air through the electroscope has been previously fully described. The only alteration made was to employ a glass capillary tube as an air-leak instead of a stopcock, as it was felt that the former was more likely to be constant in value.

The chief uncertainty in the thorium determinations arises from the small increase in leak which the solution gives in many cases. The method adopted was to measure the natural leak of the electroscope immediately before and after the rock solution. The air-supply was taken from outside the building, as the air in the laboratory is usually slightly more ionized, due to gas burners etc. The danger of the solution becoming contaminated with thorium is much less than in the case of the radium determinations, as we are dealing with so much smaller quantities in the latter case. It is highly improbable that any of the more active elements of the thorium family could be accidentally introduced, since no mesothorium preparations have ever been used in this laboratory. For a fuller description of the experimental details and the precautions adopted, the reader may refer to the earlier papers, as no important alterations have been made in the method.

In the following tables, column II. contains results obtained with the use of de-emanated carbonates.

The figures in the columns must be multiplied by  $10^{-12}$  in the case of radium and by  $10^{-5}$  in the case of thorium, the results being the quantities found per gram of rock.

In obtaining the mean values, the figures given in column I. have had to be employed in most cases. It will be seen from the results that, if de-emanated carbonates had been used in every case, the mean values would probably be reduced by about  $0.1 \times 10^{-12}$ ; not a very important alteration. It may be noticed that no thorium could be detected in the carbonates.

## BASIC ROCKS.

## Western European.

Rock.	RADIUM CONTENT.		THORIUM CONTENT.
	I.	II.	
Basaltic Lava, Iceland, near Hafna, Jordun.	0.65		0.50
Vesicular Basalt, Iceland .....	1.00		0.45
Basalt, Arthur's Seat, Edinburgh .....	1.12		1.00
Ditto .....	1.40		
Basalt, Staffa .....	0.96		0.90
Basalt with Tachylite, Tobermory, Mull.	0.96		0.60
Basalt, Squire Hill, Belfast ..	0.62		0.69
Ditto .....	0.75		0.56
Ditto .....	0.47		
Basalt, Blackhead, Co. Antrim .....	0.87	0.56	0.34
Basalt, near Clegan, Co. Galway .....	1.1		0.24
Basalt, Giant's Causeway, Co. Antrim.	0.50		0.17
Basalt, Lintz, Rhenish Prussia .....	1.50		1.26
Laminated Basalt, Striegan, Silesia ...	0.89		0.60
Basalt, Pholberg, Saxony .....	1.63		1.15
Ditto .....	1.72	1.60	
Basalt, Siebengeberge .....	1.17		1.10
Ditto .....	1.10		
Basalt, Vogelgiberge .....	1.72		1.10
Basalt, Drachenfels, Bonn .....	1.30		0.98
Gabbro, Baxenstein, Radanthal, Hartz.	1.10		0.25
Vesicular Basalt, Gravenoire Volcano, Clermont.	1.25	1.19	1.12
Basalt, Murat-le-quaire .....	1.38		0.87
Pyroxene Basalt, Les Sources de Royat, Clermont.	1.68		0.82
Clermont.	1.03		
Basalt, Mt. Rognon .....	1.03		0.56
Rowley Rag Basalt, near Birmingham.	1.13		0.71
Mean Value (a) Hebridean Basalts ...	0.77		0.49
(b) Other European Basalts	1.30		0.84

## U.S.A. (Western States).

ROCK.	RADIUM CONTENT.		THORIUM CONTENT.
	I.	II.	
Vesicular Basalt, Chaffee Co., Colorado.	1.80	1.70	1.70
Olivine Basalt, Jefferson Co., Colorado	1.86		2.40
Olivine Basalt Porphyry, Border Co., Colorado.	1.46		0.80
Ditto .....	1.55		
Hornblende Basalt, Chaffee Co., Colorado	2.70		3.00
Ditto .....	2.75		
Olivine Plagioclase Basalt, Huerfane, Co. Colorado.	1.00		1.50
Ditto .....	1.24		
Olivine Basalt, Mt. St. Helen's, Wash- ington.	1.44	1.40	0.65
Gabbro, Nye, Montana .....	1.12		0.56
Mean Value .....	1.69		1.52

## U.S.A. (Eastern States).

Diabase, Somerset Co., New Jersey ...	1.18		0.60
Diabase, Upper Mt. Clair, New Jersey.	1.12	0.80	0.83
Ditto .....	1.57		
Diabase, Columnar, Mt. Toru, Massa- chusetts.	0.85	0.71	0.60
Hornblende Gabbro, Albermarle Co., Virginia.	0.87		0.32
Ditto .....	0.83		
Quartz Diabase, Suffern, New York ...	1.22		0.90
Mean Value .....	1.09		0.65

## Atlantic Islands.

Stony Lava, St. Helena .....	1.81		1.0
Basalt, St. Helena .....	0.93	0.91	0.62
Basalt, Ascension .....	0.76		0.43
Ditto .....	0.97		
Olivine Basalt, Madeira .....	1.38		1.07
Basalt, Tenerife, Canary Islands .....	2.77	2.63	1.78
Basalt, Flores, Azores .....	1.40		0.84
Basalt, Cape Verde Islands .....	0.86		0.64
Olivine Basalt, Fernando Noronha ...	1.20		0.56
Ditto ...	1.04		
Mean Value .....	1.31		0.87

## Indian Ocean Islands.

Basalt, Christmas Island .....	1.05		0.94
Basalt, Island of Rodriguez .....	0.76		0.56
Basalt, Kerguelen Island .....	0.77		0.45
Mean Value .....	0.86		0.65



## Pacific Islands.

ROCK.	RADIUM CONTENT.		THORIUM CONTENT.
	I.	II.	
Basaltic Lava, Hawaiian Islands .....	1.25		0.28
Ropy Lava, Kilauea .....	0.96		0.30
Vesicular Basalt, Hawaiian Islands ...	1.10		0.37
Olivine Basalt, Juan Fernandez .....	1.06	0.96	0.32
Mean Value .....	1.09		0.32

## Deccan Basalts.

Index No		
20,861, Loc. Kasara-Igatpure .....	0.91	0.62
20,855, Bombay, Nagpur Ry. ....	0.75	0.43
20,851 .....	0.60	0.37
20,853 .....	0.80	0.52
20,850 .....	0.82	0.56
20,852 .....	0.72	0.24
Mean Value .....	0.77	0.46

## South African Dolerite.

Karoo Dolerite, Teviot Borehole (1225 feet deep), Cape Province.	1.75	0.58
Karoo Dolerite, near Victoria, West Cape Province.	1.25	0.62
Karoo Dolerite, Cape Province .....	1.50	0.80
Karoo Dolerite, Teviot Borehole (1025 feet deep), Cape Province.	1.25	0.79
Mean Value .....	1.44	0.70

## ULTRA-BASIC ROCKS.

ROCK.	RADIUM CONTENT.		THORIUM CONTENT.
	I.	II.	
Pierite, Cornwall .....		0.43	0.60
Pierite, Inchcolm, Firth of Forth ...		0.50	0.34
Palaeopierite, Highweek, Devonshire ..		0.44	0.32
Do. Nassau .....		0.50	0.32
Limburgite, Kaiserstuhl, Baden .....		1.20	1.40
Do. Ditto .....		1.14	
Do. Ditto .....		1.22	
Limburgite, Stoppelskuppe, Eisenach.		1.06	0.75
Do. Hassenberg, Markliss, Lausitz.		1.08	1.32
Lherzolite, Pyrenees .....		0.56	0.30
Do. Piedmont .....		0.39	0.30
Amphibole Peridotite, Schreisheim, Baden.		0.99	0.58

ULTRA-BASIC ROCKS (*continued*).

ROCK.	RADIUM CONTENT.		THORIUM CONTENT.
	I.	II.	
Biotite Peridotite, Harzburg .....		0.35	0.10
Wehrhite, Frankenstein, Odenwald ...		0.46	0.20
Hornblende Olivine Peridotite, Syracuse, New York.		1.75	1.58
Cumberlandite Peridotite, Rhode Island.	1.08		0.21
Dunite, Krombal, Styria .....		0.52	0.30
Dunite, Dun Mts., New Zealand .....		0.42	0.37
Eulysite, Tunaberg, Sweden .....		0.74	0.13
Augitite, Bohemia .....		1.40	1.37
Theralite, Sohla Mahren .....		0.96	1.12
Mean Value .....		0.80	0.61

## INTERMEDIATE ROCKS.

ROCK.	RADIUM CONTENT.		THORIUM CONTENT.
	I.	II.	
Andesite, San Juan Co., Colorado ...		2.70	1.10
Andesite Porphyry, Massachusetts ...	1.40		0.25
Granodiorite, Minnesota .....	3.15		1.57
Diorite, Sassi, Finland .....	3.06		0.47
Anorthosite, Wichita Mts., Oklahoma.	1.75		0.10
Anorthosite, New York .....	1.52		0.28
Mica Dacite, Border Co., Colorado ...	2.70		0.47
Mean Value .....	2.26		0.61

## ACID ROCKS.

(Mostly Archaean Granites.)

ROCK.	RADIUM CONTENT.		THORIUM CONTENT.
	I.	II.	
Rapakivi Granite, Finland.....	5.77		5.70
Ditto .....	6.65		6.00
Granite, Sornas, Finland .....	3.98		1.75
.. Hango, Finland .....	5.77		2.75
.. Zirkala, Finland .....	5.07		2.03
.. Haltula, Finland .....	4.72		1.75
.. Hanga Udd., Finland.....	4.62		2.25
.. Tyterlaks, Finland .....	4.81		1.37
.. Kajaloki, Finland .....	2.45		1.88
.. Orwen, Finland.....	2.97		0.75
.. Kuru, north of Tammerfors, Finland.	7.00	6.30	4.00
.. Fustila, Finland .....	4.64		8.20

ACID ROCKS (*continued*).

ROCK.	RADIUM CONTENT.		THORIUM CONTENT.
	I.	II.	
Kugel Granite, Finland .....	2.88		0.86
Granite, Flannan I-lands, W. of Lewis	1.75		0.90
Granite, Loch Michard, Sutherland ...	1.58		0.51
Granite, Cipe Wrath, Sutherland.....	2.27		1.73
Mica Gneiss, north of Tammerfors, Finland.	1.75		1.00
Adergneiss, Teisks, Finland .....	2.97		0.75
Hornblende Orthogneiss (Lewisian), Tiree.	1.20		0.64
Granogneiss, Island of Coll .....	1.84		0.52
" Ballyhaugh, Island of Coll	1.66		1.97
Orthogneiss, Tiree .....	1.60		1.63
Mean Value .....	3.54		2.31

## Broadford Sill, Skye.

Base (Basaltic) .....	0.96	0.50
10 ft. from base (Granophytic) .....	1.62	0.75
6 ft. from top (Granophytic) .....	1.49	0.52
Top (Basaltic) ... ..	1.03	0.37

## Broadford Dyke, Skye.

North Margin of Dyke (dark-coloured)	0.79	0.52
Centre of Dyke (light-coloured) .....	1.05	0.94
Ditto .....	1.75	1.08

## Dyke east of Broadford.

Easterly light-coloured margin .....	1.05	0.30
Central dark-coloured portion .....	1.92	0.64
Westerly light-coloured margin .....	1.05	0.62

The general means for basaltic rocks are as follows :—

	RADIUM.	THORIUM.
All basalts, dolerites, gabbros (58) .....	1.19	0.77
Hebridean basalts (6) .....	0.77	0.49
European " (15) .....	1.30	0.84
Deccan " (6) .....	0.77	0.46
Western U.S.A. basalts (7) .....	1.69	1.52
Atlantic Islands (8) .....	1.31	0.87
Indian Ocean Islands (3) .....	0.86	0.65
Pacific " " (4) .....	1.09	0.32
Eastern U.S.A. " (5) .....	1.09	0.65
S. African (4) .....	1.44	0.70

Results previously available as determined by similar methods of analysis (Phil. Mag. October 1912 and April 1915) :—

	RADIUM.	THORIUM.
All basalts, dolerites, gabbros (31) .....	1·28	0·51
Hebridean basalts (11) .....	0·50	0·38
Basalts, Deccan and Antarctic (14) .....	2·0	0·84
Diabases and dolerites (8) .....	1·0	0·22
Gabbros and norites (5) .....	1·3	0·50
General basalts (18) .....	1·4	0·63

On similar rocks, but determined by the Wet Method, the radium content was as follows :—

	GABBROS AND NORITES.	DOLERITES AND DIABASES.	BASALTS.
Strutt <sup>1</sup> .....	0·63 (1)	0·59 (2)	0·44 (8)
Farr and Florence <sup>2</sup> .....	0·33 (2)	0·59 (3)	0·81 (1)
Buchner <sup>3</sup> .....	0·70 (1)	0·87 (2)	0·50 (1)
Fletcher <sup>4</sup> .....	...	...	0·71 (5)

<sup>1</sup> Strutt, Proc. R. S. lxxvii. & lxxxiv.

<sup>2</sup> Farr & Florence, Phil. Mag. Nov. 1909.

<sup>3</sup> Buchner, *Konink. Akad. Wet. Amsterdam*, Oct. 1910 and April 1911.

<sup>4</sup> Fletcher, Phil. Mag. July 1910 and Jan. & June 1911.

Comparing the new results with the previous results obtained by similar procedure, there is little difference noticeable. Thus 58 basalts, dolerites, and gabbros give for the radium content 1·19 (recent), and 31 similar rocks formerly give 1·28. In the thorium content on the same specimens we have: recent 0·77 and former 0·51. The radium results by Wet Method are hardly comparable; they have been shown by direct comparison to give somewhat lower values. The published results show values ranging from 0·33 to 0·87 for rocks of basaltic origin.

The chief matter of interest is the values to be ascribed to the plateau basalts. Daly, Washington, and others have shown that there is close chemical resemblance between the chemical composition of the plateau lavas, and among these, the Deccan, Thulean (Hebridean), and Oregonian (Western U.S.A.) are specifically cited by Washington. The radioactive constituents are closely alike in quantity in the case of the Hebridean and Deccan, but the basalts from the Western U.S.A. show appreciably greater quantities both of

radium and of thorium. If the latter specimens are authentically derived from the plateau basalt, this is difficult to account for.

The point is of interest, for as we would naturally infer the plateau basalts to represent the general basaltic substratum of the earth's surface, the evaluation of their average radioactivity is of importance. On the other hand, the lavas of the oceanic islands might be expected to proceed from pockets in the lava forming the ocean-floor which possibly do not take part in the phenomena of the cyclical changes and deformation of the earth's surface crust.

In short, we want to know, so far as may be attainable, what quantities of radioactive materials are to be taken into account in forming an estimate of the time-periods involved in the evolution of heat in the substratum. This is the most important constant connected with the geological influence of radioactivity. It is hoped to continue the present investigation, with a view to derive, if possible, further light on this point as well as on the subject of small errors possibly entering into the existing procedure.

The ultra-basic rocks are somewhat lower in the mean than the basalts. These rocks have, hitherto, not been systematically investigated.

A point of interest is the high values noticeable in the case of certain of the granites of Finland. There appears to be no doubt of the reliability of these results; they apply to areas where intense thermal conditions prevailed in remote times.

A comparison of the results for acid, intermediate, and basic rocks shows that the relation first found by Lord Rayleigh is sustained.

We have to thank Dr. J. J. Sederholm for the specimens from Finland and for information most kindly supplied therewith. We desire to acknowledge also the kindness of Professor Harold S. Palmer in sending lavas from Hawaii, and of the Trustees of the British Museum in supplying specimens from the oceanic islands.

LXXXI. *Crystal Structure and Absorption Spectra.*—*The Cobaltous Compounds.* By ROBIN HILL and OWEN RHYS HOWELL\*.

[Plate XXV.]

**T**HE red and blue colours of the cobaltous compounds have attracted much attention and many theories have been advanced to account for them and for the change from one to the other.

Von Babo (*Jahresber.* 1857, p. 72) appears to have been the first to observe the change in colour of cobalt solutions on heating and on the addition of alcohol or of certain salts. He thought the transformation from red to blue was due to dehydration of the cobalt salt. Schiff (Liebig's *Ann. Chem.* ex. p. 203, 1859) was of the same opinion. Gladstone (*Journ. Chem. Soc.* x. p. 79, 1858; *ibid.* xi. p. 36, 1859) after examining the spectra of cobalt solutions, and Vogel (*Ber.* xi. p. 913, 1878) after a more extended investigation, also inferred that the difference in colour was due to a difference in hydration. Russell (*Proc. Roy. Soc.* xxxii. p. 258, 1881) studied the absorption spectra of various cobalt solutions and of fused cobalt salts, and he concluded that the change in colour was due to the presence of hydrates. Tichborne (*Chem. News*, xxv. p. 133, 1872), Potilitzin (*Ber.* xvii. p. 276, 1884; *Bull. Soc. Chim.* (3) vi. p. 264, 1891), Lescoeur (*Ann. Chim. Phys.* (6) xix. p. 547, 1890; *ibid.* (7) iv. p. 213, 1895), Étard (*Comptes Rendus*, cxiii. p. 699, 1891; *ibid.* cxx. p. 1057, 1895), Charpy (*Comptes Rendus*, cxiii. p. 794, 1891), and Wyruboff (*Bull. Soc. Chim.* (3) v. p. 460, 1891; *ibid.* vi. p. 3) studied the formation and range of stability of the hydrates of different cobalt salts. They argued from their results that the change in colour on heating was best explained by a change from one hydrate to another.

Hartley (*Trans. Roy. Dub. Soc.* (2) vii. p. 253, 1900; *Journ. Chem. Soc.* lxxxiii. p. 401, 1903) made a very exhaustive investigation on the absorption spectra of cobalt solutions at different dilutions and at different temperatures. He found that those salts which are anhydrous, or are not dehydrated below 100°, or do not change colour when dehydrated, give solutions whose absorption spectra do not change on heating. Hydrated salts, however, give solutions whose absorption spectra undergo a marked change on

\* Communicated by the Authors.

heating, and a similar change is generally produced by the addition of salts which act as dehydrating agents. Hartley therefore concluded that the change in colour is essentially an hydration phenomenon. Jones and Uhler (*Amer. Chem. Journ.* xxxvii. p. 126, 1907) have examined the absorption spectra and electrical conductivities of cobalt solutions in the presence of varying amounts of different salts. They found that "the blue and red colours correspond, respectively, to wide and narrow bands; or, in terms of the theory, to small hydration and relatively large hydration."

This theory of hydration is sufficient to account for the colour changes within its limited application. It is, however, not sufficiently embracing in that it makes no attempt to account for the colour of anhydrous compounds and of solids.

Berch (*Wien. Akad. Sitzungsber.* (2) lvi. p. 724, 1867), thinking he observed a transformation of the red  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  to blue without change of composition, proposed to account for the change in colour of cobalt salts by postulating that there are two modifications of the hexahydrate, one red and the other blue. Potilitzin (*loc. cit.*) showed that the observation was incorrect and thus disproved the theory. Not only has this view no experimental justification, but it contributes nothing towards an explanation of the cause of the colour.

Ostwald (*Grundlinien der anorg. Chem.* p. 620; *Lehrbuch der allgem. Chemie*) believes the red colour is due to the cobalt ion and the blue colour to the un-ionized salt. Whereas this may explain the change in colour from red to blue on the addition of certain salts to cobalt solutions, by consequent depression of the ionization of the cobalt salt, it fails to explain why some salts are ineffective in bringing about the change. It also fails to account for the change in colour on heating, since the ionization of the salt undergoes very little change in the process.

Engel (*Bull. Soc. Chim.* (3) vi. p. 239, 1891; see also Le Chassevent and Le Chatelier, *ibid.* (3) vi. pp. 3, 84, 209, 1891) considers that no general theory can explain all the colour changes. Each one must have a separate interpretation. The change in colour of cobalt chloride solution on the addition of hydrochloric acid or metallic chlorides is due to the formation of double chlorides in solution.

Donnan and Bassett (*Journ. Chem. Soc.* lxxxi. p. 939, 1902) from a study of the coloured solutions, chiefly their behaviour on electrolysis, concluded that "the blue colour is largely due to complexes such as  $\text{CoCl}_4$  or  $\text{CoCl}_3$ ," while the red colour is due to "the cobalt atom outside the immediate

sphere of the chlorine atoms." The colour of a solution containing cobalt and another metal is consequently determined by the relative tendencies of the two metals to form complex anions. If the cobalt has the greater tendency, the solution is blue; if the other metal has the greater tendency, the solution is red.

Hantzsch and Shibata (*Zeit. anorg. Chem.* lxxiii. p. 309, 1912) determined the apparent molecular weight and the absorption spectrum of cobalt thiocyanate in various solvents. From the manner of ionization thus determined, they concluded that the blue solutions contained *complexes* such as  $\text{Co}[\text{Co}(\text{SCN})_4]$  in which the cobalt atom in the complex is associated with four groups, and the red solutions contained complexes such as  $\text{Co}[\text{Cl}_4(\text{HgCl}_2)_2]$  or  $[\text{Co}(\text{SCN})(\text{H}_2\text{O})_5]\text{SCN}$  in which the cobalt atom in the complex is associated with six groups.

The interest of the present authors was aroused in this subject by a chance observation through a direct vision spectroscope that the absorption spectra of cobalt spinel, cobalt blue, and the blue solution of cobalt oxide in potash were so very similar. In the present communication an account is given of the absorption spectra in the visible region of a number of cobaltous solutions and of pigments derived from divalent cobalt. The latter are an important class of compounds which do not appear to have been investigated hitherto in this way, nor does any attempt appear to have been made to account for the colour of cobalt solutions by comparing them with the solid compounds.

Working along these lines, we have concluded that the blue colour is due to the direct association of the cobalt atom with four atoms or groups, and that the red colour is due to its direct association with six atoms or groups. We were led to this belief before we were aware of the paper by Hantzsch and Shibata (*loc. cit.*), who assign similar values to the number of groups forming their complexes. As will appear, our idea of the nature of the four and six associations is entirely different and is applicable generally. Thus, whereas the hypothesis of Hantzsch and Shibata can hardly be used to account for the colour of the pigments, our own idea of the association in solution is founded on the constitution of these. Again, Hantzsch and Shibata assume that the addition of a metallic salt to a solution of a cobalt salt results in the formation of a complex between the two salts; we show that the function of the added salt is simply to force the cobalt atom from one type of association to the other.



## EXPERIMENTAL.

*Preparation of Pigments.*—A number of compounds in which cobaltous oxide is combined with certain colourless oxides are well known pigments. The essential method of preparation consists in heating a mixture of the oxides to obtain a homogeneous non-fused mass. It is, however, advantageous to use the sulphates, because on warming they melt in their water of crystallization giving a perfect mixture, and on further heating evolve sulphur dioxide yielding a friable and completely oxidized mass. Our method of preparation, therefore, consisted in making a mixture of the requisite quantities of the sulphates (or stannic oxide and silica where these enter the composition) and heating, gently at first and finally at about  $1200^{\circ}$  for half an hour.

As ordinarily prepared for pigments, these compounds are too intensely coloured for examination. We therefore prepared "diluted" colours in which the cobalt is replaced by other suitable metals such as magnesium or zinc. In each case a series was prepared. The compound at the one end of the series, containing no cobalt, was used as a "blank"; the compound at the other end of the series, containing the maximum possible amount, was prepared to see if it was of the same nature as the intermediate compounds, and it was compared with the corresponding commercial "artist's" colour. One of the intermediate compounds of suitable intensity was selected for examination.

The following is a list of the pigments prepared, together with the composition of the "diluted" compound examined:—

Thénard's Blue or			
Cobalt Blue	(a)	$\text{CoOAl}_2\text{O}_3$	$32 \text{ MgOAl}_2\text{O}_3$
" "	(b)	$\text{CoOAl}_2\text{O}_3$	$32 \text{ BeOAl}_2\text{O}_3$
" "	(c)	$\text{CoOAl}_2\text{O}_3$	$32 \text{ ZnOAl}_2\text{O}_3$
Cerulean Blue	(a)	$\text{CoOSnO}_2$	$32 \text{ MgOSnO}_2$
" "	(b)	$(\text{CoO})_2\text{SnO}_2$	$32(\text{MgO})_2\text{SnO}_2$
" "	(c)	$(\text{CoO})_2\text{SnO}_2$	$32(\text{ZnO})_2\text{SnO}_2$
Cobalt o-silicate	(a)	$(\text{CoO})_2\text{SiO}_2$	$4(\text{MgO})_2\text{SiO}_2$
" "	(b)	$(\text{CoO})_2\text{SiO}_2$	$32(\text{ZnO})_2\text{SiO}_2$
Rimann's Green		$\text{CoO } 2.56 \text{ ZnO}$	
Cobalt Pink		$\text{CoO } 8 \text{ MgO}$	

*Preparation of Solutions.*—The coloured solutions were made by adding the requisite quantity of a concentrated standard solution of cobalt sulphate to a solution of the potassium salt saturated at room temperature, or to hydrochloric acid saturated with the necessary metallic chloride.

The corresponding "blank" solution was made up in the same way using water instead of the cobalt solution. Both solutions were allowed to stand in order that the precipitated potassium sulphate and suspended particles might settle.

The "cobalt thiocyanate in ether" was made by extracting a solution containing a known amount of cobalt, treated with potassium thiocyanate, with ether containing 5 per cent. of amyl alcohol until colourless, and making up the extracts to a known volume.

The concentration of each solution is given in brackets after it and is expressed as gram atoms of cobalt per litre.

*Instrument.*—All the measurements were made by means of a Nutting photometer with a Hilger Wavelength Spectroscope.

The pigments were examined by reflected light. Small boxes were made of cardboard in the form of a cube with two of its adjacent faces missing. One of these boxes was placed immediately against each of the photometer apertures with one of the open sides next the aperture and the other open side up. The inside of one of the boxes was covered with a thick layer of the pigment and the other with a corresponding "blank," both prepared by mixing with 5 per cent. gum arabic solution to the necessary consistency. The source of light was a powerful half-watt lamp placed immediately above the photometer box.

For the examination of the liquids the optical arrangement of the instrument as ordinarily employed was slightly modified by using as a light source a disk of opal glass placed in front of a 200 candle-power half-watt lamp, and by inserting a lens in each of the two beams (formed on division) to bring the image of the light source into the plane of the rhomb, a suggestion kindly made by Dr. Hartridge. With this arrangement the relative intensities of the three fields did not vary with the position of the eye at the eyepiece; moreover, the coincidence in the junction of the fields was rendered more perfect owing to elimination of diffraction.

*Cell.*—It was deemed advisable, where the solubility of the substance allowed, to examine a thin layer of concentrated cobalt solution in preference to a thick layer of dilute solution, for the following reasons:—

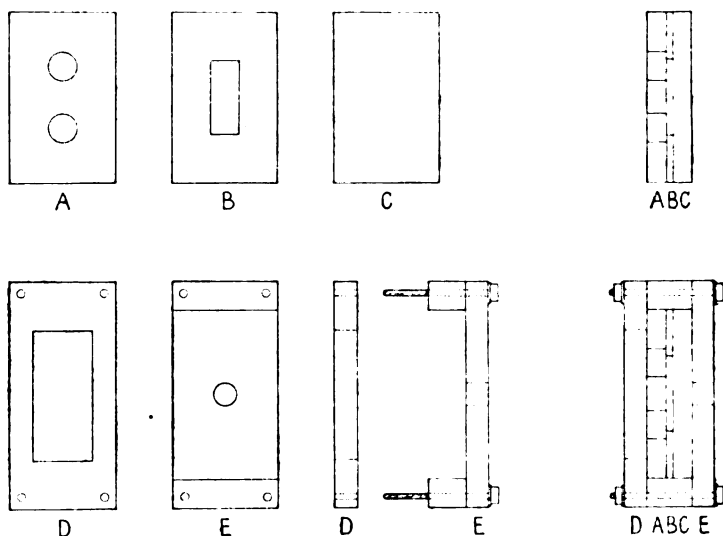
(a) The effect of any impurities in the potassium salt used for making the solutions is of less account.

(b) The effect of oxidation or of other changes in the coloured solution is greatly reduced.

(c) The loss of light due to suspended particles is of less consequence.

A special cell was therefore designed and constructed as shown in fig. 1. A and C are two pieces of plate glass 6 cm.  $\times$  3.7 cm.  $\times$  7 mm. A has two holes each 1 cm. diameter bored through it, their centres being 2.3 cm. apart. B is a piece of window glass the same size as A and C, but only 2 mm. thick, and has a square hole 2.6 cm.  $\times$  9 mm. cut in the middle. A B and C are put together face to face as shown, the faces in contact being smeared with a very little vaseline. The whole is held in a wooden frame made of two pieces D and E. D has a square hole 4.6  $\times$  2 cm. cut in it

Fig. 1.



giving sufficient clearance to the two holes in A. E is provided with four small bolts as shown; it has a hole 8 mm. diameter bored through the middle. The assembled cell is placed in E, D is placed over it, and the whole screwed up.

The holes in A are provided with rubber stoppers carrying glass tubes, the lower leading to a stoppered flask containing the solution for examination and the upper to a receiver. The solution is blown over, filling the cell. The tubes are so arranged that the beam of light is uninterrupted; it enters A between the two holes, traverses the layer of liquid and emerges through the hole in E which gives a beam of the requisite size without any stray light.

Two such cells were mounted side by side on a stand, the distance between them being such that the two emerging beams coincided with the apertures of the photometer box. One was filled with the cobalt solution and the other with the "blank."

*Method of Plotting.*—All the curves are plotted with wavelengths in Ångström units as abscissæ and fraction of light absorbed as ordinates.

### *Blue Compounds.*

The crystal structure of spinel ( $\text{MgO Al}_2\text{O}_3$ , or  $\text{Mg Al}_2\text{O}_4$ ) has been elucidated by means of X-rays by W. H. Bragg (Phil. Mag. (2) xxx. p. 309, 1915), who showed that each magnesium atom is surrounded by *four* oxygen atoms. In this connexion it may be noted that Dickinson (Journ. Amer. Chem. Soc. xlv. p. 774, 1922) has shown from an X-ray examination of the crystal structure of the double alkali cyanides of cadmium and mercury ( $\text{K}_2\text{Cd}(\text{CN})_4$  and  $\text{K}_2\text{Hg}(\text{CN})_4$ ) that the groups  $\text{Cd}(\text{CN})_4$  and  $\text{Hg}(\text{CN})_4$  play the same part in the structure as the  $\text{MgO}_4$  group in spinel.

The magnesium atoms in spinel may be partly replaced by cobalt, giving the blue cobalt spinel. We are indebted to Mr. A. Hutchinson, F.R.S., for a piece of the artificial gem which we used for examination.

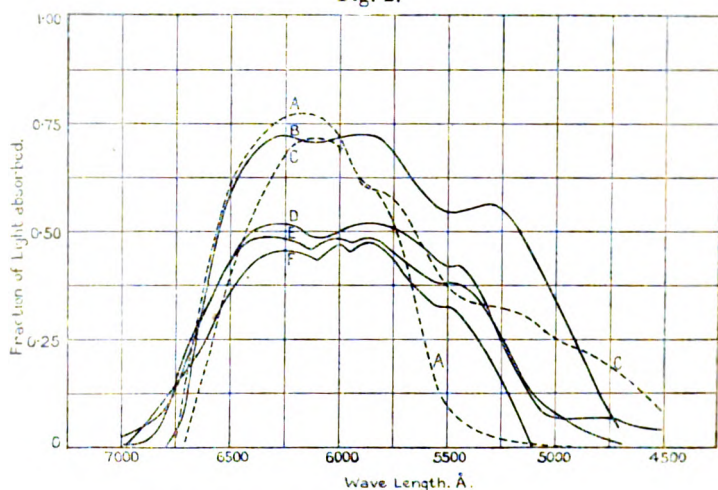
It will be seen that the curves for cobalt spinel (fig. 2 F) and cobalt blue (fig. 2 E) are almost identical, the only difference in their form being that the maxima in the case of the spinel are sharper than in that of the cobalt blue, since the former is examined by transmitted light and the latter by reflected light, where some is scattered. It is therefore reasonable to conclude that the structure of cobalt blue is identical with that of cobalt spinel. Since cobalt spinel is a solid solution, it follows that in both cases the cobalt atom replaces the magnesium atom without change in structure and is therefore surrounded by four oxygen atoms.

The absorption curve for cobalt blue with beryllium as diluent (fig. 2 D) is of precisely the same nature as with magnesium as diluent. On treating this substance with concentrated acids the cobalt is readily dissolved, leaving a perfectly white residue of beryllium aluminate (crysoberyl). It follows that cobalt aluminate and beryllium aluminate are non-miscible and that the absorption spectrum of this pigment is due to the cobalt aluminate itself contained in it. Since the same absorption spectrum is obtained with cobalt blue, confirmatory evidence is thus obtained that in this

compound cobalt and magnesium are interchangeable without change in structure.

Zinc is known to form a spinel with the same structure as magnesium spinel, and it may be replaced by cobalt yielding a blue pigment just as magnesium is so replaceable. The

Fig. 2.



- A. Cobalt thiocyanate in ether.  $\left(\frac{1}{20,000}\right)^*$ .  
 B. Cobalt oxide in potassium hydroxide.  $\left(\frac{1}{40}\right)$ .  
 C. Cobalt thiocyanate in potassium thiocyanate.  $\left(\frac{1}{40}\right)$ .  
 D. Cobalt Blue (b).  $\text{CoO Al}_2\text{O}_3 \cdot 32\text{BeO Al}_2\text{O}_3$ .  
 E. Cobalt Blue (a).  $\text{CoO Al}_2\text{O}_3 \cdot 32\text{MgO Al}_2\text{O}_3$ .  
 F. Cobalt Spinel.

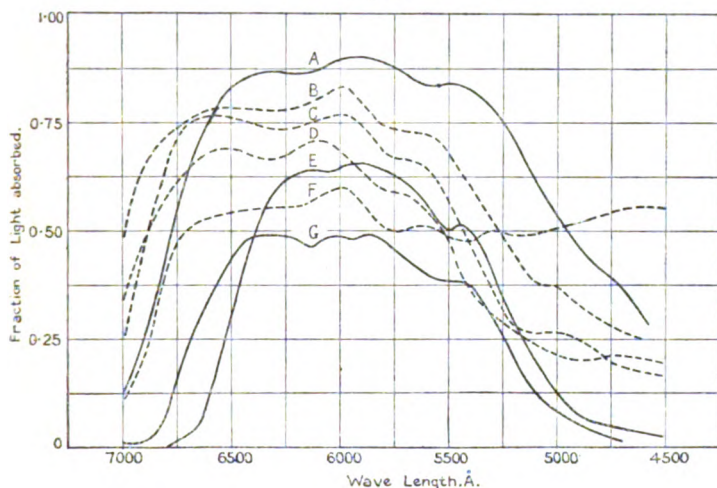
\* Examined in 10 cm. tube.

absorption spectrum of this compound (fig. 3 E) is strictly comparable with that of cobalt blue with magnesium as diluent (reproduced again for comparison in fig. 3 G). The absorption bands are exactly similar. The compound is of a more violet shade than the corresponding magnesium one. This is particularly noticeable in artificial light, the magnesium compound retaining more of the blue colour than the zinc compound. This fact is interesting because it is stated that zinc oxide is added in the manufacture of commercial cobalt blue. Its effect is not to introduce a tinge of green into the blue colour as is popularly supposed, but only to help in forming the spinel structure. The curves bring out

this point and show that the effect on the absorption spectrum of introducing zinc for magnesium is extremely slight, thus clearly revealing the  $\text{CoO}_4$  group as a distinct entity.

Cerulean blue is stated to be a compound of cobalt oxide and stannic oxide. It has been investigated by Hedvall (*Arkiv. Kem. Min. Geol.* (18) v. p. 1, 1914), who prepared

Fig. 3.



- A. Cobalt ortho-silicate (b).  $(\text{CoO})_2\text{SiO}_2 \cdot 32(\text{ZnO})_2\text{SiO}_2$ .  
 B. Cerulean Blue (b).  $(\text{CoO})_2\text{SnO}_2 \cdot 32(\text{MgO})_2\text{SnO}_2$ .  
 C. Cerulean Blue (a).  $\text{CoO} \cdot \text{SnO}_2 \cdot 32\text{MgO} \cdot \text{SnO}_2$ .  
 D. Rinmann's Green.  $\text{CoO} \cdot 256\text{ZnO}$ .  
 E. Cobalt Blue (c).  $\text{CoO} \cdot \text{Al}_2\text{O}_3 \cdot 32\text{ZnO} \cdot \text{Al}_2\text{O}_3$ .  
 F. Cerulean Blue (c).  $(\text{CoO})_2\text{SnO}_2 \cdot 32(\text{ZnO})_2\text{SnO}_2$ .  
 G. Cobalt Blue (a).  $\text{CoO} \cdot \text{Al}_2\text{O}_3 \cdot 32\text{MgO} \cdot \text{Al}_2\text{O}_3$ .

cobalt ortho-stannate  $\text{Co}_2\text{SnO}_4$  which he found was green, but that if more stannic oxide was used the product became bluer in proportion to the excess employed. We first tried using calcium as a diluent in this case and obtained a semi-fused greyish-blue mass. It was obvious that the compound was of a totally different type; calcium cannot replace cobalt without change in structure of the compound.

By introducing an equivalent amount of magnesium for cobalt in the ortho-stannate, however, a perfectly blue product is obtained which corresponds exactly in colour and intensity with the artist's pigment "cerulean blue." It is seen that this compound (fig. 3 B) has precisely the same

absorption spectrum as one having double the amount of stannic oxide (fig. 3 C). It therefore follows that in both cases the cobalt is present as the ortho-stannate; the function of the excess of stannic oxide must be the same as that of the magnesium oxide.

By introducing zinc instead of magnesium, a dull green compound is obtained. This would appear to correspond more nearly to the green pure ortho-stannate, since the atomic weight of zinc is approximately the same as that of cobalt. It will be seen, however, that the absorption spectrum of this compound (fig. 3 F) is exactly similar to that of the other two stannates with an additional absorption in the violet.

The absorption spectrum of cobalt oxide in zinc oxide (fig. 3 D) is of exactly the same shape as in the case of the stannates. The compound was examined against zinc oxide as a "blank." The zinc oxide was prepared under the same conditions as the pigment and was a distinct yellow. Although the pigment is a bright green (Rinmann's Green) its absorption spectrum examined in this way is precisely the same as that of the perfectly blue stannates. Further, the absorption spectra of all these compounds are exactly like those of the cobalt blues, the only difference being that they are a little more extended.

Now the crystal structure of zinc oxide has been elucidated by W. L. Bragg (Phil. Mag. xxxix. p. 647, 1920) by X-ray measurements, and he showed that the zinc atom is surrounded by four oxygen atoms. The cobalt atom replacing the zinc is consequently similarly situated, and there seems no doubt, therefore, that in all these compounds the cobalt atom is surrounded by four other atoms.

Cobalt hydroxide is readily soluble in hot concentrated potassium hydroxide, yielding an intense blue solution from which it crystallizes in pink microscopic crystals (de Schulten, *Compt. Rend.* cix. p. 266, 1889). It may be noted that magnesium hydroxide similarly dissolves in and crystallizes from hot concentrated potash (de Schulten, *ibid.* ci. p. 72, 1885). The absorption spectrum of the cobalt solution (fig. 2 B) is of exactly the same character as that of cobalt spinel and cobalt blue, so that the cobalt atom appears to be similarly enveloped in all cases. It is suggested that in the solution of cobalt oxide in potash the cobalt atom is also surrounded by four groups, probably hydroxyls.

*The persistence of a definite association of groups or a molecular structure in solution just as in solids seems to be very real.*

The absorption spectrum of cobalt thiocyanate in potassium thiocyanate (fig. 2 C) bears a marked resemblance to that of the oxide in potash. The second and third bands are depressed but correspond exactly with those of the latter.

In the case of the thiocyanate in ether (fig. 2 A) the second band has almost disappeared and the third completely. A difference is to be expected since this is a solution of a simple cobalt salt; the cobalt atom is uncharged. The close similarity of this curve to that of the thiocyanate in potassium thiocyanate is therefore all the more striking.

Both in the blue solids and blue solutions, therefore, the cobalt atom is in immediate association with *four* atoms or groups.

### *Red Compounds.*

The structure of magnesium oxide has been investigated by Wyckoff (Amer. Journ. Sci. i. p. 138, 1921), who found it was of the same type as that of rock-salt; the magnesium atom is surrounded by *six* oxygen atoms. Cobalt replaces the magnesium in the oxide, giving a *red* compound. The cobalt atom is here surrounded by six oxygen atoms and the absorption spectrum (fig. 4 F) is of an entirely different type from that of the blue pigments. It is suggested that just as in the blue compounds the colour is due to the association of the cobalt atom with four groups, so also in the red compounds the colour is due to its association with six.

Although the absorption spectrum of potassium cobaltocyanide  $K_4Co(CN)_6$  has not been examined owing to the rapidity with which it decomposes water, it is interesting to note that the solution is pink and that the compound is described as violet-red crystals. Here the cobalt atom is known to be associated with six cyanogen groups.

The chloride, sulphate, and nitrate of cobalt give practically identical absorption spectra (fig. 4 A) at the dilution used, and the form of the curve is exactly similar to that of cobalt oxide in magnesium oxide. It follows that the cobalt atom is associated with six groups in these solutions. Since the salts are almost completely ionized, it would appear that the cobalt atom is in direct association with six molecules of water.

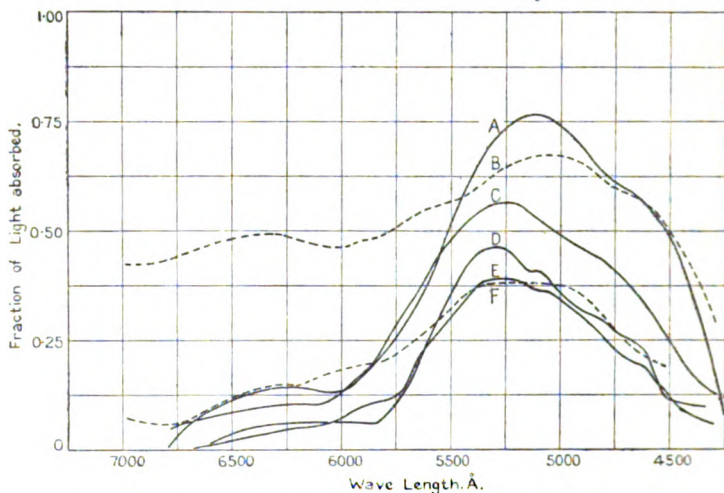
The absorption spectra of the formate (fig. 4 E), oxalate (fig. 4 D), and tartrate (fig. 4 C) in the corresponding potassium salts are all strictly comparable with each other and with those of cobalt oxide in magnesium oxide and the aqueous solutions of the chloride, sulphate, and nitrate. It



therefore appears that the cobalt atom is similarly associated with six groups in these solutions also.

The cobalt ortho-silicate with magnesium as diluent is *red* and gives a very similar absorption spectrum (fig. 4 B) to that of cobalt oxide in magnesium oxide. With zinc as diluent, however, the compound is *blue* and gives an absorption spectrum (fig. 3 A) absolutely comparable with that of

Fig. 4.



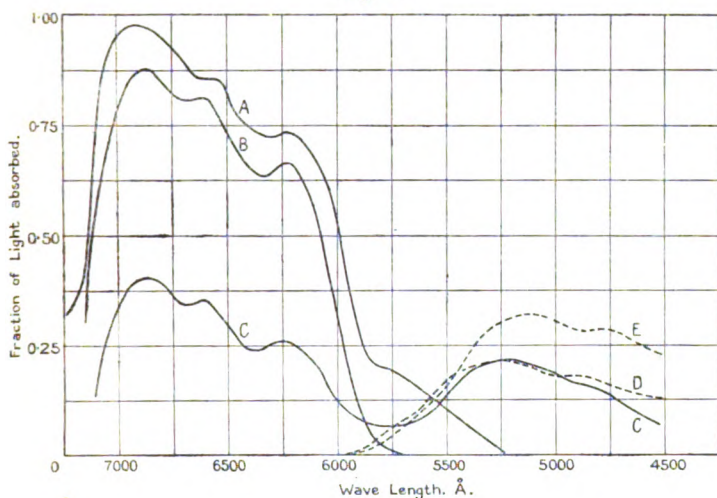
- A. Cobalt chloride, sulphate, or nitrate.  $\left(\frac{1}{50}\right)^*$ .  
 B. Cobalt ortho-silicate (a).  $(\text{CoO})_2\text{SiO}_2 \cdot 4(\text{MgO})_2\text{SiO}_2$ .  
 C. Cobalt tartrate in potassium tartrate.  $\left(\frac{1}{10}\right)$ .  
 D. Cobalt oxalate in potassium oxalate.  $\left(\frac{1}{10}\right)$ .  
 E. Cobalt formate in potassium formate.  $\left(\frac{1}{10}\right)$ .  
 F. Cobalt Pink.  $\text{CoO} \cdot 8\text{MgO}$ .

\* Examined in 10 cm. tube.

cobalt blue. It is evident that the two compounds are of entirely different structure. It would appear that in the former the cobalt atom replacing the magnesium is associated with six groups. In the latter, the zinc atom which has a strong tendency towards association with *four* groups is so situated and the cobalt atom replacing it takes the same structure, yielding a blue compound.

The absorption spectrum of cobalt in concentrated hydrochloric acid (fig. 5 A) is of very similar shape to that of cobalt oxide in zinc oxide (fig. 3 D) but shifted bodily into the red. It is therefore probable that the cobalt atom is similarly situated and associated with four atoms (or groups), possibly chlorine. The behaviour of the solution on the addition of other salts confirms this.

Fig. 5.



- A. Cobalt chloride in hydrochloric acid.  $\left(\frac{1}{5000}\right)^*$ .  
 B. Cobalt chloride in  $HCl + MgCl_2$ .  $\left(\frac{1}{100}\right)$ .  
 C. Cobalt chloride in  $MgCl_2$  alone.  $\left(\frac{1}{10}\right)$ .  
 D. Cobalt chloride in  $HCl + ZnCl_2$ .  $\left(\frac{1}{10}\right)$ .  
 E. Cobalt chloride in  $ZnCl_2$  alone.  $\left(\frac{1}{5}\right)$ .

\* Examined in 10 cm. tube.

The addition of magnesium chloride to the solution causes no change of colour, and the absorption spectrum (fig. 5 B) is almost identical. The addition of zinc chloride, however, changes the colour from blue to red, and the absorption spectrum (fig. 5 D) becomes exactly comparable with that of cobalt oxide in magnesium oxide. In other words, the cobalt atom which was previously associated with *four* atoms is now associated with *six*. The change would appear to be

due to the superior tendency of the zinc to associate with four atoms ; there is a redistribution of the structure, whereby the zinc atom takes to itself four groups and the cobalt atom, as a result, has six forced upon it.

The same distribution occurs with zinc chloride alone in the absence of hydrochloric acid, and a precisely similar absorption spectrum is shown (fig. 5 E). With magnesium chloride alone in the absence of hydrochloric acid, however, a particularly interesting result is obtained. Although the solution remains blue, the absorption spectrum (fig. 5 C) shows that both the red and blue compounds are present together. The curve is composed of two distinct parts, the one being the typical curve obtained with the blue compounds and the other that with the red. Since the intensity of the blue compounds is far greater than that of the red, it will be seen from the curve that very little blue is present compared with the red, although the solution looks blue. In the case of magnesium, therefore, which is not strictly limited to an association with four groups, as is zinc, the general structure as regards the cobalt atoms has not been displaced to one form alone ; in fact, both are seen to be present in equilibrium.

Some representative spectra are reproduced in the Plate, and we are indebted to Mr. F. J. Stoakley for invaluable aid in preparing the photographs.

#### SUMMARY.

1. By examining and comparing the absorption spectra of solutions with those of solid compounds of known crystalline structure, the nature of the association of the atoms in solution can be elucidated.

2. The cobalt atom in the solid *blue* compounds is associated with *four* other atoms or groups. The same arrangement accounts for the colour of the blue solutions.

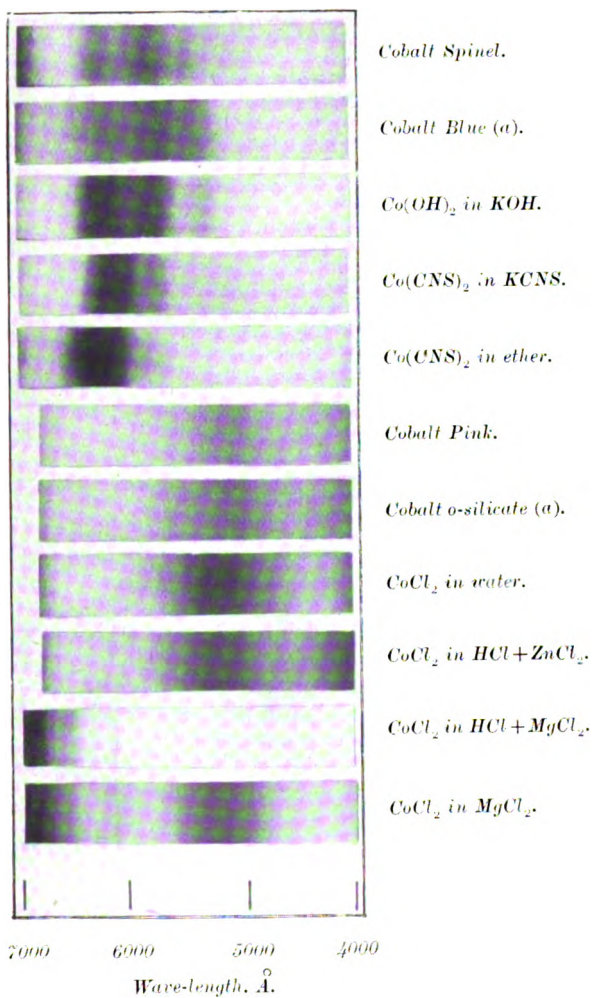
3. Similarly, in the solid *red* compounds and in the red solutions the cobalt atom is associated with *six* other atoms or groups.

4. The blue compounds are more soluble than the red ; the latter usually separate from solution.

5. The maximum absorption of the blue compounds is much greater than that of the red.

6. Constitutions are given to the well known cobaltous pigments.

We are deeply indebted to Mr. C. T. Heycock for placing at our disposal the necessary apparatus in the Goldsmiths'





Laboratory for the preparation of the pigments, and to Professor T. M. Lowry for giving us exceptional facilities for making the spectroscopic measurements. One of us (O. R. H.) is indebted to the Royal Commissioners for the Exhibition of 1851 and the other (R. H.) to the Board of Scientific and Industrial Research, for grants held during this investigation.

University Chemical Laboratory,  
Cambridge.

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LXXXII. *The Damping of Torsional Vibrations in Air at Reduced Pressures.* By RUBY V. WAGNER, M.Sc. \*

THE Law of Maxwell, that the viscosity of a gas is independent of the pressure, is known to hold only within certain limits of pressure, and to break down completely at exhaustions greater than about  $1/60$  atmosphere. A convenient method of investigating the relation between the viscosity and the pressure is by observation of the damping of torsional vibrations at different pressures, the logarithmic decrement for such vibrations being a function of the viscosity. This method was employed by Crookes, Maxwell, and others, various forms of vibrating body being used.

In the experiments of Crookes† a mica vane was suspended in a vertical plane and made to oscillate about its vertical diameter, the damping being observed at pressures ranging from atmospheric to  $0.2 \times 10^{-6}$  atmosphere.

A different arrangement was used by Maxwell‡ in the experiments made to test the validity of his law. He suspended a circular disk in a horizontal plane between two fixed plates, the disk oscillating in its own plane about the axis of the suspension, thus exposing a larger surface to the frictional forces.

Experiments were made with similar apparatus by Kundt and Warburg§, and the deviations from the law at higher

\* Communicated by Prof. W. Wilson, Ph.D. The experimental work described in this paper formed the subject of a thesis approved for the M.Sc. degree of the University of London.

† Crookes, Phil. Trans. clxxii. p. 387.

‡ Clerk Maxwell, Scientific Papers, ii. p. 1.

§ Kundt and Warburg, Pogg. Ann. clv. p. 340 (1875).

exhaustions were examined. In their earlier work no accurate measurements of pressure were made, and the apparent diminution in the gas viscosity was ascribed entirely to the sliding of the gaseous layers over the oscillating body, the coefficient of slip being inversely proportional to the pressure, and thus producing the same effect as a reduction in the viscosity.

A modified form of this apparatus was used by Hogg\*, who showed that the decrease in viscosity is a real effect, and that the reduction in damping cannot be accounted for entirely by the slip. He used a McLeod gauge for measurements of pressure, and obtained curves for various gases.

More recently experiments have been carried out† in which the stationary deflexions of a body, caused by the rotation of a neighbouring body, were measured at different pressures. This method is open to the objection that for high exhaustions large speeds of rotation are necessary, and these set up irregular conditions in the gas and increase the disturbing effects of slight deviations from parallelism etc.

In the experiments here described the measurement of the logarithmic decrement was preferred, a hollow aluminium cylinder being used as oscillating body in place of the mica or glass disks of earlier experiments. This cylinder is very light, and the damping due to the suspension should be very small in comparison with that due to air friction.

A hollow aluminium cylinder was suspended by a bifilar silk suspension between two concentric brass cylinders, an air-gap of about 2 mm. separating the oscillating body from each of the stationary ones. The oscillations were started magnetically, and the damping observed by means of a beam of light reflected on to a scale by a small concave mirror above the cylinder.

When the pressure is such that the mean free path of the molecules is small compared with the distance between the cylinders, the relation between the logarithmic decrement and the viscosity can be calculated as for a liquid. The equation to the oscillation is

$$I \frac{d^2\theta}{dt^2} + \left( 2\pi a^3 h \mu \frac{d_1 + d_2}{a_1 d_2} \right) \frac{d\theta}{dt} + \eta \theta = 0, \quad . \quad . \quad (1)$$

\* J. L. Hogg, "On Friction in Gases at Low Pressures," *Amer. Acad. Proc.* xlii. no. 6, pp. 115-146 (July 1906); xlv. no. 1, pp. 3-17 (Aug. 1909).

† Timiriazeff, "Ueber die Innere Reibung Verdünneter Gase," *Ann. der Phys.* xl. pp. 971-991. Langmuir, *Phys. Rev.* April 1913.

where  $I$  = moment of inertia of the system,  
 $a$  = radius of oscillating cylinder,  
 $h$  = height of oscillating cylinder,  
 $\mu$  = coefficient of viscosity,  
 $d_1 d_2$  = distance between the oscillating and each of  
the stationary cylinders,  
 $\eta$  = the torsion constant.

The logarithmic decrement

$$\lambda = \frac{\pi^2 a^3 h \mu (d_1 + d_2)}{\sqrt{\eta I} \cdot d_1 d_2}, \quad \dots \dots \dots (2)$$

$$i. e. \quad \lambda = A \frac{d_1 + d_2}{d_1 d_2} \mu, \quad \dots \dots \dots (2 a)$$

$$i. e. \quad \lambda \propto \mu.$$

At low pressures, when the mean free path is comparable with the distance  $d$ , it cannot be assumed that the velocity of the gas layer is the same as that of the solid in contact with it, and allowance must be made for the slip.

Maxwell defines the coefficient of slip as the quantity  $\beta = \frac{\mu}{\sigma}$ ,

where  $\mu$  = the coefficient of viscosity and  $\sigma$  = coefficient of external friction, *i. e.* the force required per unit area of plane to maintain a uniform relative velocity of 1 cm./sec.

The resistance to the moving body is then the same as if the fixed surface was moved back a distance  $2\beta$ , and allowance can be made for the slip by writing  $(d + 2\beta)$  instead of  $d$ , the quantity  $\beta$  being inversely proportional to the pressure (Kundt and Warburg).

The decrement  $\lambda$  is then no longer proportional to the viscosity, for, substituting  $(d + c/p)$  for  $d$  in the expression (2 a),  $c$  being a constant, and  $p$  = pressure,

$$\lambda = A \mu p \left( \frac{1}{p d_1 + c} + \frac{1}{p d_2 + c} \right).$$

The suspended cylinder A (fig. 1) was of thin aluminium sheeting, 0.5 mm. thick, radius 2.05 cm., height 2.5 cm., with struts across the top as in the figure (fig. 2), the struts and cylinder being cut from a spun cylindrical aluminium box, so that there were no joints. At the centre of the

*Phil. Mag.* S. 6. Vol. 48. No. 287. Nov. 1924. 3 L



cross formed by the struts a small hole was pierced, into which was fitted a thin aluminium rod (*b*, fig. 2) about 2.5 cm. long, and shaped into a hook at the upper end. This rod was held in place by a small nut below the struts, and to it was fixed a small concave mirror (*c*), at the back of which was attached a very small piece of magnetized watch-spring.

Fig. 1.

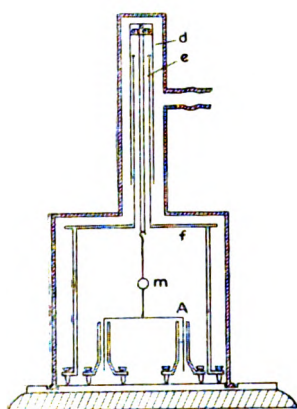
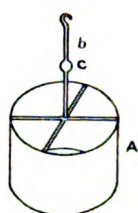
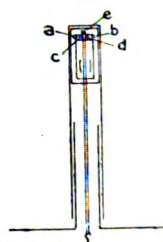


Fig. 2.



The bifilar suspension (fig. 3) was the same as that used in the White pattern of the Kelvin quadrant electrometer. *e* is a conical screw which can be moved in or out of its socket, thus separating or approaching the screws *c*, *d*, round which the fibre passes. By turning the pins *a*, *b*, the suspension can be lengthened or shortened, and the points of suspension can be moved forwards or backwards by means of the same screws. The silk fibre passed round the hook on *b* (fig. 2), which was grooved to prevent slipping.

Fig. 3.



The upper part of the bifilar was fixed to a hollow brass cylinder (*d*, fig. 1) sliding over a second cylinder *e*, about 1 cm. diameter and 10 cm. long, through which the fibres passed. This cylinder was supported on a circular brass plate *f* standing on three legs with screw feet, the plate having a hole at the centre, 1 cm. in diameter, to allow the suspension to pass through. The bifilar could be made of suitable length by sliding the outer cylinder up or down, and final adjustments were made by means of the

pins *c*, *d*. The bifilar was arranged to give a convenient period of oscillation, that finally used being 18 secs.

The stationary cylinders were also of brass, and stood on three legs with screw feet. The oscillating cylinder projected by about 2 mm., above and below the two brass cylinders, which were of equal height. This arrangement facilitated the adjustments and setting for parallelism, and made it possible to view the oscillating cylinder after the case was sealed down.

The containing chamber was entirely of brass, and cylindrical in shape, as shown in fig. 1. In the lower part a plate-glass window 3.5 cm. by 6.5 cm. was sealed on to a ground rim with Faraday cement. The exit tube was in the upper part of the case, so that the oscillating system was in some measure protected in case of a sudden inrush of air.

The base consisted of a brass plate, in which grooves were cut for the screw feet, the plate being fixed to a wooden base, and the whole standing on a slate slab projecting from the wall.

The cylinders were placed in position, and the bifilar so arranged that the addition of the small magnet produced no change in the zero reading. There was therefore no twist on the bifilar in the position of rest. The necessary adjustments of level were made by means of the screw feet.

The general arrangement of the apparatus was as indicated in fig. 4. *B*, *C* are drying tubes filled with phosphorus pentoxide, which could readily be renewed by opening the tubes *h*, *k*. The tube *D* contains vegetable charcoal, and *E*, *F* are McLeod gauges. *G* leads to a Fleuss-Geryk oil-pump.

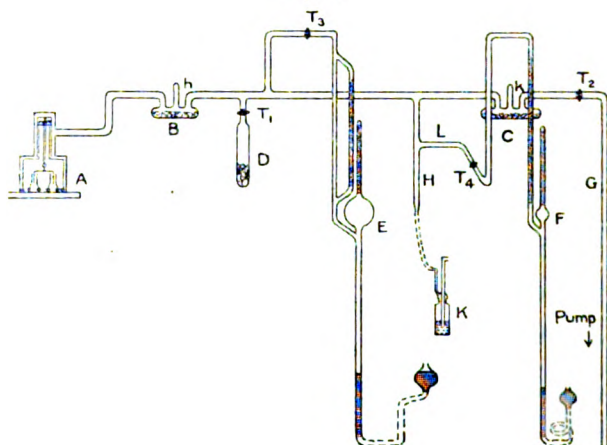
The joint to *A* was sealed with Faraday cement, and a pressure tubing sleeve was found satisfactory at the pump, as the tap *T*<sub>2</sub> was kept closed at higher exhaustions. The brass case and window were sealed down with cement. The tube *H* was drawn into a capillary and sealed off. Dry air was admitted when necessary through the wash-bottle *K* containing concentrated sulphuric acid.

As a preliminary precaution, the apparatus was repeatedly evacuated and filled with dry air. It was then sealed up, evacuated to about 0.2 mm., and the charcoal in *D* alternately strongly heated and cooled *in vacuo*. The oil-pump was worked by an electric motor, and pressures from atmospheric to 0.15 mm. could be obtained. Pressures below these were obtained by immersing the charcoal tube *D* in liquid oxygen. By means of the tap *T*<sub>1</sub> the charcoal tube

could be placed in communication with the rest of the apparatus for any requisite length of time, and the exhaustion proceeded with by stages, pressures between 0.015 cm. and 0.00001 cm. being readily obtained.

The use of liquid oxygen has an advantage over that of liquid air in that the temperature of the boiling liquid remains constant, whereas in the case of liquid air a fresh supply, being richer in nitrogen, will have a lower temperature than a quantity that has been standing for some hours\*.

Fig. 4.



For measurements of pressure between 76 cm. of Hg and 1 cm. Hg, the McLeod gauge F was replaced by an ordinary manometer. Pressures below 1 cm. were read by means of a McLeod gauge with a bulb of about 30 c.c. capacity; and for pressures below 0.015 cm., a McLeod with a 500 c.c. bulb was used. The upper readings of the gauge F could also be taken with the manometer, and the lower readings of F with the McLeod E, so that the readings on the various gauges could be made to overlap, and continuity was ensured. The decrement was measured at pressures ranging from atmospheric to 0.00001 cm. Hg.

The required pressure was obtained by means of the pump or liquid oxygen, and the taps  $T_1$ ,  $T_2$  were closed. The apparatus was then left for about ten minutes. (This was

\* J. L. Hogg, Amer. Acad. Proc. xlv. (Aug. 1909).

found necessary, as otherwise the pressure in A was not the same as that indicated by the gauge at the lower pressures, and unreliable readings resulted.) The pressure was then read on the McLeod gauge. The oscillations were started by bringing up a small magnet to the case A, and 20 complete oscillations read by means of a lamp and scale at a distance of 1 metre from A. The decrement was calculated from these. The pressure reading was then again taken, and if it varied from the earlier measurement, the readings were discarded.

The experiments were carried out at room temperature, which was read at intervals, and accordingly it was desirable to cover as large a pressure range as possible each day. The small changes in temperature during the day did not appreciably affect the results, and except at the highest exhaustions, curves obtained on days when the temperatures differed by  $1^{\circ}$  or  $2^{\circ}$  C. coincided.

Two distinct sets of readings were taken. In one case the outer brass cylinder only, and in the second case both outer and inner brass cylinders, were used.

The results obtained are indicated in the accompanying tables and curves, the curves being drawn from readings taken on different days and selected so that, as far as possible, the temperature was constant throughout. For the section below 0.001 cm. two sets of readings only were used, when the temperature was the same as for the other readings. The logarithmic decrement  $= l \times \log_e 10$ , and the ordinates in the curves represent  $l$ .

The entire range can be shown most conveniently by plotting logarithms of pressures as abscissæ, and values of  $l$  as ordinates (curve 1). Sections are shown in the following curves (pp. 856, 857).

(A) *For the case when the outer brass cylinder only was used.*

Kundt and Warburg state\* that as long as the layer of gas has thickness greater than fourteen times the mean free path, the retarding force does not vary by more than 1/1000 part of its value. In the curves obtained, however, the decrement is seen to fall off quite decidedly from 76 cm. to about 30 cm. Hg. This effect was noted by Crookes in the case of all gases except hydrogen.

\* Kundt and Warburg, Phil. Mag. July 1875.

Between 30 cm. and 1.5 cm. the decrement is constant, then falls off slowly to 0.15 cm. and more rapidly afterwards. At about 0.015 cm. the mean free path becomes approximately equal to the distance between the cylinders, and the

TABLE (Curve A).

P. (cms. Hg).	<i>l</i> .	log P.
77.15	.03787	1.88733
73.75	.03778	1.86777
66.35	.03751	1.82184
55.05	.03699	1.74075
47.85	.03659	1.67989
42.35	.03635	1.62685
33.95	.03615	1.53085
26.8	.03598	1.42813
14.35	.03583	1.15686
8.75	0.589	.94201
4.05	.03578	.60745
1	.03555	.00000
.644	.03553	1.96567
.3134	.0352	1.53577
.2002	.0349	1.20140
.1357	.03452	1.13268
.06763	.03305	2.83014
.02882	.02991	2.45983
.02236	.02879	2.3496
.01548	.02621	2.18986
.01409	.02553	2.14895
.01146	.02367	2.05922
.01112	.02340	2.04621
.00968	.02244	3.98588
.00732	.0204	3.86392
.00678	.0198	3.83108
.00442	.0164	3.64561
.00298	.0136	3.47420
.00220	.01221	3.34242
.00140	.00933	3.14516
.001115	.00845	3.04725
.00076	.0070	4.88080
.00059	.0055	4.76938
.00041	.00536	4.61287
.00034	.00483	4.53148
.00016	.00389	4.20412
.000078	.00315	5.89209
.000053	.00304	5.72423
.000034	.00264	5.53148
.0000184	.00251	5.26482
.000011	.00242	5.04287

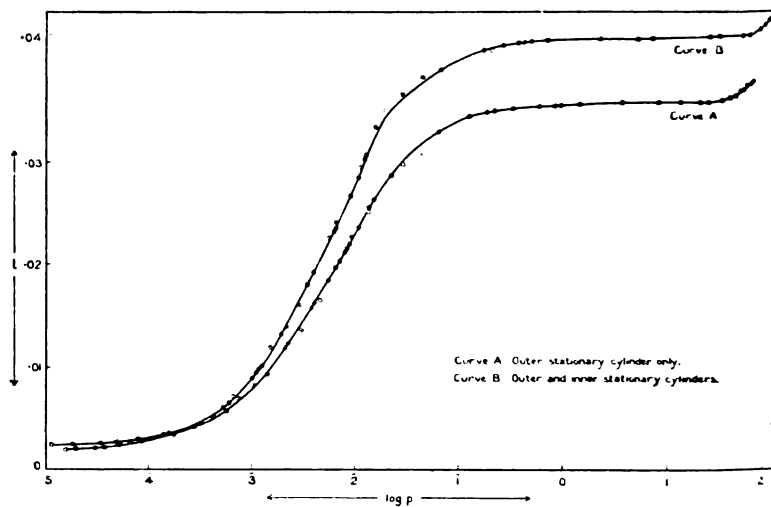
TABLE (Curve B).

P. (cms. Hg.).	$\lambda$ .	log P.
76.53	.04250	1.88384
60.73	.04240	1.78341
36.2	.04225	1.55871
28.73	.04221	1.45834
8.13	.04207	.91909
5.53	.04206	.74273
2.63	.04197	.41996
.77366	.04192	1.88855
.53159	.04180	1.72558
.28009	.04155	1.44730
.19276	.04109	1.28502
.06945	.03915	2.84167
.04769	.03821	2.67839
.03143	.03652	2.49723
.01989	.02532	2.29859
.01616	.03356	2.20845
.01294	.03044	2.11206
.01099	.02842	2.04107
.00973	.02710	3.98833
.00680	.02397	3.83277
.00421	.01937	3.62467
.00356	.01807	3.55189
.00282	.01596	3.45025
.00224	.01392	3.35025
.00175	.01199	3.24304
.00124	.00974	3.09202
.00069	.00697	4.83885
.000616	.00659	4.78958
.00053	.00601	4.72428
.000316	.00462	4.49969
.00023	.00427	4.36173
.000156	.00348	4.19312
.000068	.00307	5.83505
.000064	.00286	5.80618
.000052	.00259	5.71600
.000036	.00233	5.55630
.000019	.00217	5.27875
.000015	.00212	5.18184

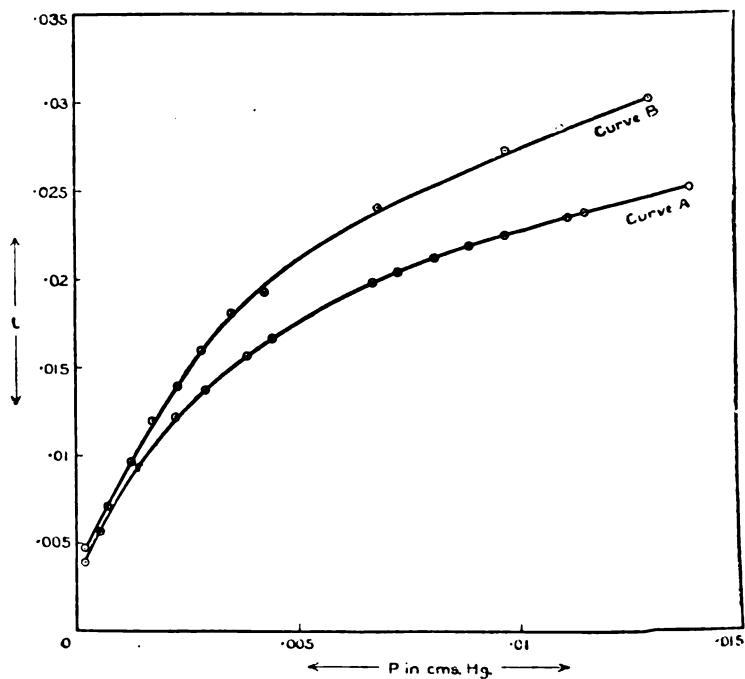
Values for Curve 3 B (calculated).

P. (cms. Hg.).	$\lambda$ .
.0136	.0295
.0103	.0274
.00921	.0265
.0076	.025
.00584	.0225
.0044	.0200
.00339	.0175
.00255	.015
.00129	.01
.000729	.00697

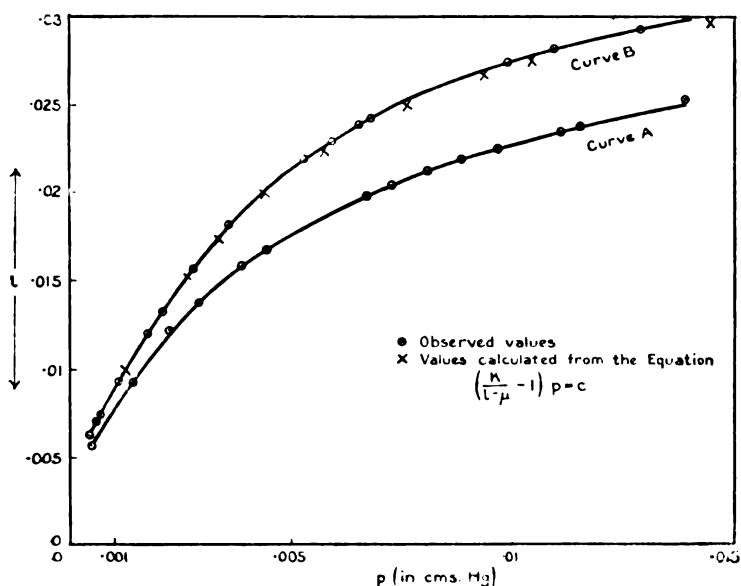
Curve 1.



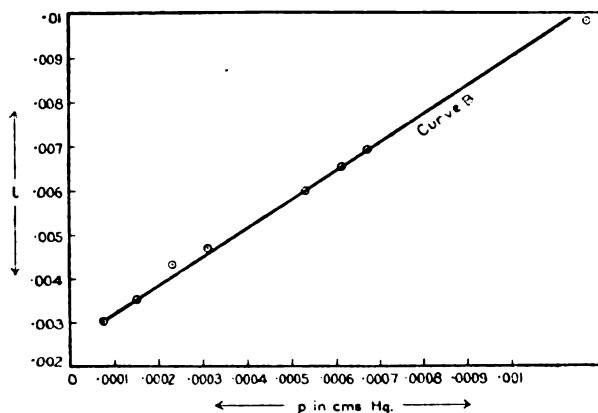
Curve 2.



Curve 3.



Curve 4.



decrement then falls off very rapidly (curve 2). In the logarithmic curve there is a point of inflexion, and the decrement appears to approach a constant value, about .05 of its value at atmospheric pressure. This residual damping will be due to the friction in the silk fibre, and possibly in a



very small degree to electromagnetic effects. Hogg takes the limiting value for  $l$ , as determined from his curves, to indicate the damping due to causes other than air friction, and allows for the viscosity of the suspension etc. in this way.

Below about 0.0007 cm. the decrement is proportional to the pressure. This fact has been utilized \* in the construction of gauges for the measurement of low pressures in cases where the use of a McLeod is undesirable. A gauge of the decrement type was first suggested by Sutherland †, and various types have since been developed ‡.

(B) *For the case when the outer and inner brass cylinders were used.*

In this case, only a very slight decrease in the damping was observed at pressures just below atmospheric, and the decrement remained almost constant down to a pressure of about 1.5 cm. Attempts were made to find whether the decrease noticeable in curve A occurred at slightly higher pressures in curve B. The brass case was soldered to the base with Wood's fusible alloy, and the window wired on to the case. A manometer and pump were connected to the oscillation apparatus, and the readings thus carried up to about 130 cm. Hg. A slight increase in the decrement was found as indicated in Curve 1.

The region between 0.015 cm. and 0.0005 cm. is shown in curve 2. The earlier equations of Maxwell and Sutherland were modified by Hogg to the expression

$$\left\{ \frac{k}{l-\mu} - 1 \right\} p = c,$$

where  $k$  and  $c$  are constants,

$l$  = the total logarithmic decrement,

$\mu$  = the decrement due to the suspension etc.,

which Hogg took as the lowest value of  $l$  obtained in his experiments, the constants being calculated from the curves.

This equation holds very accurately for curve B for pressures below 0.015 cm., suitable values, as determined

\* P. E. Shaw, Proc. Phys. Soc. Lond. xxix. pp. 171-175. Langmuir, Phys. Rev. April 1913.

† Sutherland, Phil. Mag. Feb. 1897.

‡ S. Dushman, "Production and Measurement of High Vacua."

from the curves, being given to the constants  $k$  and  $c$ . The calculated and observed values are shown in curve 3, the values taken for the constants being

$$k = \cdot 0372, \quad c = \cdot 0047, \quad \mu = \cdot 002.$$

At pressures below  $\cdot 001$  cm. the mean free path becomes greater than the distance  $d$ . Collisions between the molecules are infrequent, and they travel to and fro between the oscillating and stationary cylinders, the angular momentum of the oscillating cylinder being thereby reduced. The loss of momentum will be proportional to the number of molecules present, *i. e.* to the pressure, and to the mean molecular velocity, which is constant as long as the temperature is constant. The logarithmic decrement will accordingly be proportional to the pressure\*. This was found to be the case, the linear relation holding for pressures about  $\cdot 0007$  cm.

Curve B crosses curve A in curve 1 at about  $\cdot 0002$  cm. It would appear that at these and lower pressures a large proportion of the damping is due to the suspension, and the two curves would be expected ultimately to coincide. It was unfortunately not possible to employ the same suspension in the two sets of readings; for curve B a new suspension was used, which was adjusted so that the decrement at atmospheric pressure was the same as for the previous suspension under the same conditions. The difference between the two suspensions would show more markedly at high exhaustions, and the fact that the lowest value of  $l$  in curve B is greater than in curve A can be accounted for by this difference.

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LXXXIII. *A Note on the Theory of Artificial Telephone and Transmission Lines.* By The Research Staff of the General Electric Co., Ltd.† (*Work conducted by A. C. BARTLETT.*)

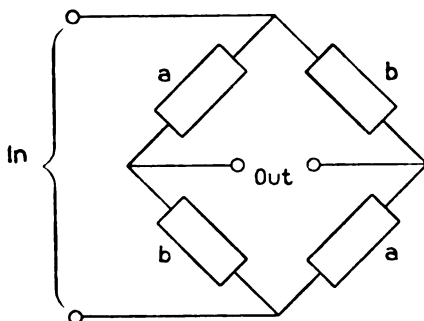
A UNIFORM telephone line of length  $l$  having inductance  $L$ , resistance  $R$ , capacity  $C$ , and leakage  $S$  per unit length can be replaced, as far as measurements at the two ends are concerned, by various simple networks, of

\* Dushman, "Production and Measurement of High Vacua," Part 4, General Electrical Review, Sept. 1920.

† Communicated by the Director.

860 Research Staff of the G. E. C., London, on the  
which one is illustrated in fig. 1,

Fig. 1.



where

$$a = Z_0 \coth \frac{Pl}{2},$$

$$b = Z_0 \tanh \frac{Pl}{2},$$

$$Z_0 = \sqrt{R + jpL} / \sqrt{S + jpC},$$

$$P = \sqrt{R + jpL} \cdot \sqrt{S + jpC},$$

$$p = 2\pi f,$$

$f$  being the frequency.

In other networks of this kind impedances appear which are represented by hyperbolic sines and cosecants in addition to tangents and cotangents. The methods discussed in this note have not, so far, proved applicable to such networks.

The elements of these networks such as  $Z_0 \tanh \frac{Pl}{2}$  can be represented at any given frequency by a resistance in series with either a capacity or an inductance, but such a representation is not correct at all frequencies.

In practice, when a long artificial line has to be simulated, it is usually split up into a number of short lengths  $\frac{l}{n}$ . In this case  $\frac{Pl}{2n}$  is small so that

$$\begin{aligned} Z_0 \tanh \frac{Pl}{2n} &= Z_0 \cdot \frac{Pl}{2n} \\ &= (R + jpL) \cdot \frac{l}{2n}, \end{aligned}$$

which is a resistance  $\frac{Rl}{2n}$  in series with an inductance  $\frac{Ln}{2n}$ ; the values are independent of frequency, provided  $\frac{l}{n}$  is sufficiently small.

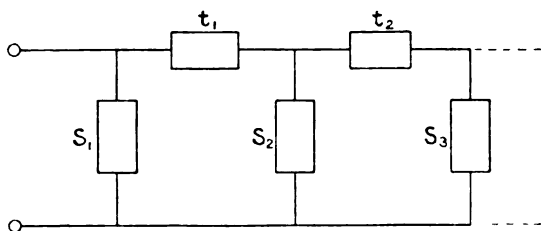
The purpose of this note is to put forward an alternative method which does not require the line to be split into small sections; its interest is perhaps theoretical rather than practical. It depends on the expansion of  $Z_0 \tanh \frac{Pl}{2}$  and  $Z_0 \coth \frac{Pl}{2}$  either as an infinite continued fraction or as an infinite series such that the terms of the fraction or series can be represented by simple arrangements of resistances, inductances, and capacities.

First we have

$$\begin{aligned} \tanh x &= x - \frac{x^3}{3} + \frac{x^5}{5} - \dots, \\ Z_0 \tanh \frac{Pl}{2} &= \frac{Z_0 \frac{Pl}{2}}{1 + \frac{\frac{Pl}{2}^2}{3} + \frac{\frac{Pl}{2}^4}{5} + \dots} \\ &= \frac{1}{\frac{2}{Z_0 Pl} + \frac{1}{3 \cdot 2 Z_0} + \frac{1}{5 \cdot 2 Z_0} + \dots}, \\ &\text{and so on.} \end{aligned}$$

But this represents the impedance of the network,

Fig. 2.



where

$$\begin{aligned} S_n &= \frac{Z_0 Pl}{2(4n-3)}, \\ t_n &= \frac{Z_0}{Pl} \cdot 2(4n-1). \end{aligned}$$

Now

$$Z_0 Pl = l(R + jpL),$$

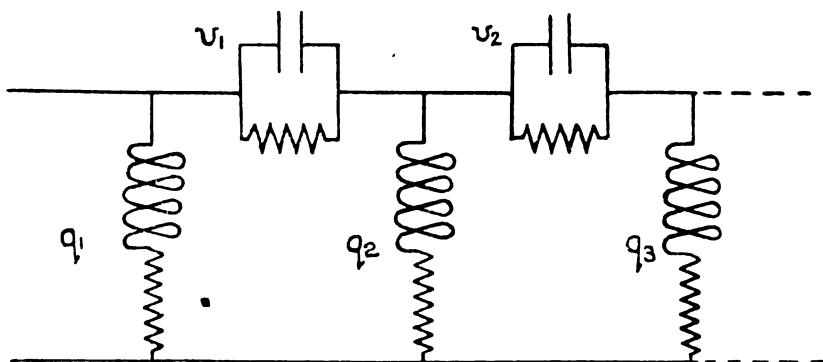
and is therefore a resistance  $lR$  in series with an inductance  $lL$ ; and

$$Z_0/Pl = \frac{1}{l(S + jpC)},$$

a capacity  $lC$  shunted by a leak  $lS$ .

Thus  $Z_0 \tanh \frac{Pl}{2}$  can be represented by the network,

Fig. 3.



the shunt elements being given by

$$q_n = \frac{l}{2(4n-3)} \cdot (R + jpL);$$

the series elements by

$$v_n = \frac{2(4n-1)}{l(S + jpC)}.$$

Second we have

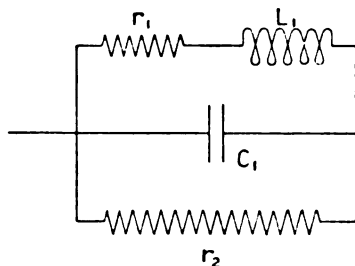
$$\tanh u = \sum_{n=1}^{n=\infty} \frac{8u}{(2n-1)^2 \pi^2 + u^2}.$$

Thus  $Z_0 \tanh \frac{Pl}{2}$

$$\begin{aligned} &= \sum \sqrt{\frac{R + jpL}{S + jpC}} \cdot \frac{4l \sqrt{R + jpL} \cdot \sqrt{S + jpC}}{(2n-1)^2 \pi^2 + l^2 (R + jpL)(S + jpC)} \\ &= \sum \frac{1}{\frac{(2n-1)^2 \pi^2}{4l(R + jpL)} + \frac{(S + jpC)l}{4}}. \end{aligned}$$

But the expression under the  $\Sigma$  is the impedance of the network,

Fig. 4.



where

$$r_1 = \frac{4/R}{(2n-1)^2\pi^2},$$

$$L_1 = \frac{4/L}{(2n-1)^2\pi^2},$$

$$r_2 = \frac{l}{4},$$

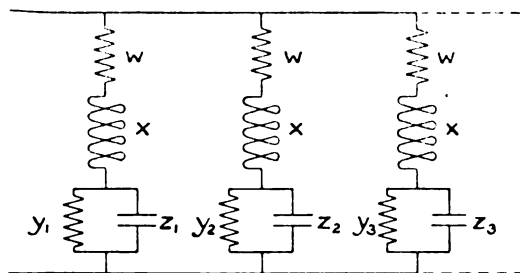
$$C_1 = \frac{4}{lS}.$$

Thus  $Z_0 \tanh \frac{Pl}{2}$  can be represented by an infinite series of such networks connected in series.

The other elements of the network of fig. 1 can be treated by applying the foregoing analysis to the admittance instead of to the impedance.

$Z_0 \coth \frac{Pl}{2}$  is equivalent to the following network if the series expansion is used,

Fig. 5.



where

$$w = \frac{R}{4},$$

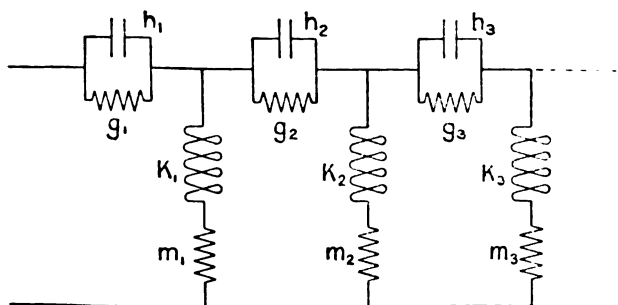
$$x = \frac{lL}{4},$$

$$y_n = \frac{1}{4lS} \cdot (2n-1)^2 \pi^2,$$

$$z_n = \frac{4lC}{(2n-1)^2 \pi^2}.$$

If the continued fraction expansion is used, it is equivalent to

Fig. 6.



where

$$h_n = \frac{lC}{2 \cdot (4n-3)},$$

$$g_n = \frac{2(4n-3)}{lS},$$

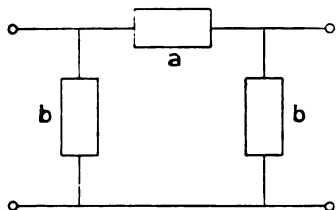
$$k_n = \frac{lL}{2(4n-1)},$$

$$m_n = \frac{Rl}{2(4n-1)}.$$

Thus all the elements of the "bridge" type of network shown in fig. 1 can be expanded into convergent forms that are physically realizable, and any desired approximation can be obtained by taking a sufficient number of terms.

We have not succeeded in obtaining similar expansions for the impedance  $Z_0/\sinh Pl$  and  $Z_0 \sinh Pl$  that occur in the  $\Pi$  and  $T$  types of artificial line illustrated in fig. 7.

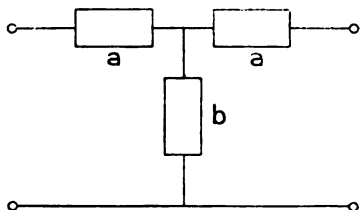
Fig. 7.



Π Section.

$$a = Z_0 \sinh Pl.$$

$$b = Z_0 \coth \frac{Pl}{2}.$$



T Section.

$$a = Z_0 \tanh \frac{Pl}{2}.$$

$$b = Z_0' \sinh Pl.$$

In connexion with this it is interesting to note that  $Z_0 \tanh \frac{Pl}{2}$  and  $Z_0 \coth \frac{Pl}{2}$  have definite physical meanings, being the impedances of a line of length  $\frac{l}{2}$  short circuited and open circuited respectively at the far end, whereas  $Z_0 \sinh Pl$  and  $Z_0/\sinh Pl$  have no such definite meaning.

*Note added later.*

The expansion

$$\coth x = \frac{1}{x} + \sum \frac{2x}{x^2 + n^2\pi^2}$$

can also be used and gives networks of the same general form for

$$Z_0 \coth \frac{Pl}{2} \text{ and } Z_0 \tanh \frac{Pl}{2}.$$

Thus both

$$Z_0 \coth \frac{Pl}{2} \text{ and } Z_0 \tanh \frac{Pl}{2}$$

can be expanded either in the form of a ladder network or as an infinite sequence of impedance elements connected in parallel or as an infinite sequence of impedances connected in series.



LXXXIV. *On Air-waves of Finite Amplitude.* By W. B. MORTON, M.A., and AMY I. WOODS, M.A., M.Sc., Queen's University, Belfast\*.

#### INTRODUCTION.

THE classical memoir on this subject is that published in 1910 by the late Lord Rayleigh †. In it a thorough examination is made of the conditions under which it is possible for a disturbance of finite amplitude to be propagated through a gas without change of type. After a summary and criticism of the earlier work of Poisson, Stokes, Earnshaw, Rankine, and Hugoniot, the conclusion is reached, by combining arguments of a mechanical and thermodynamic kind, that such propagation is only possible when the influence of dissipative forces is taken into account and when the wave is one of compression, bringing a higher density to a region of the gas. Further, the wave is of a very special type; an assigned ratio of initial and final pressures must be accompanied by a definite ratio of densities also, and therefore of temperatures, and there must be a definite relative velocity of the two masses of gas which are separated by the wave.

Lastly, the possibility of the physical existence of the wave is conditional on the existence of a solution, satisfying the terminal conditions, of a certain rather complicated differential equation, involving the variation of the specific volume along the wave. An equation, exactly equivalent to this, but using the velocity as dependent variable, was arrived at independently by Mr. G. I. Taylor ‡ in a paper read at the same meeting of the Royal Society.

In the earlier part of Lord Rayleigh's paper the effects of heat-conduction and viscosity are considered separately, but both are taken into consideration in the final discussion which leads to the equation. It does not appear to be necessary to make the separation, since the two magnitudes are linked together by the theory of gases.

Lord Rayleigh established the existence of the required solution by a closely-reasoned and rather difficult argument, based on an interpretation of the differential equation as an equation of motion of a particle. By way of confirmation he worked out two special cases arithmetically by the method of Runge. It seemed possible to discuss this matter in a

\* Communicated by the Authors.

† Proc. Roy. Soc. lxxxiv. p. 247 (1910); Collected Papers, v. p. 573.

‡ Proc. Roy. Soc. lxxxiv. p. 371 (1910).

somewhat broader way by means of the graphical method of "isoclines," of which an account is given by M. D'Ocagne in his book '*Calcul Graphique et Nomographie*'\*, where Massau is named as the originator of the method. This is done in the first part of the present paper.

In the second part the physical characteristics of the "Rayleigh wave" are examined in some detail. It seems worth while to do this in spite of the very special nature of this type of motion, and the improbability of the precise balance of terminal states, needed for its unchanging advance, being attained in practice. Actual explosion waves have often been photographed. Probably the observation of a wave has not been extended through a sufficiently great distance to permit of the detection of change of form. It does not appear impossible that by some kind of adjustment the permanent type is approached as the wave proceeds. At any rate, this special type may present some features in common with the more general case of a wave initiated in an arbitrary manner.

# I. THE RAYLEIGH-TAYLOR EQUATION.

In Lord Rayleigh's form the equation is

$$\mu' \frac{d}{dx} \left( \mu' \frac{dr^2}{dx} \right) + \mu' \frac{dr^2}{dx} \left\{ \frac{3(\gamma+1)}{8\gamma} \cdot \frac{v_1+v_2}{c} - \frac{3}{2} - h \right\} \\ = \frac{3}{4} h (\gamma+1) (v_1 - v) (v - v_2)$$

(*loc. cit.*, eqn. 98).

$v$  is the volume of unit mass, decreasing, as the wave passes, from  $v_1$  to  $v_2$ ;  $\gamma$  is the ratio of specific heats and  $h$  the constant  $c\mu/k$ , where  $c$  is the specific heat at constant volume,  $\mu$  the viscosity, and  $k$  the conductivity;  $\mu'$  is the viscosity divided by the mass-velocity  $m$ , i. e. the mass which crosses unit area per second at any point, when the wave is made stationary in space by superposing the proper backward velocity on the gas as a whole. For the discussion which follows it is convenient to adopt a transformation of the equation differing slightly from Lord Rayleigh's. We shall put

$$-\mu' dr^2/dx = v_2^2 \eta, \quad v = v_2 \xi, \quad v_1/v_2 = s,$$

so that  $\xi$  is the specific volume expressed as a multiple of its ultimate value and  $s$  is used, as in Rayleigh's paper, for the ratio of the final to the initial density. The dependent variable  $\eta$  is the ratio of increase of  $\xi^2$  in the small distance  $\mu'$ ,

\* P. 149. See also an article by Erodetsky in the '*Mathematical Gazette*,' 1919-20.

measured in the direction in which the wave is travelling. Rayleigh's  $(\xi, U)$  correspond to our  $(v_1^2 \xi^2, -v_2^2 \eta)$ . The equation now takes the form

$$\frac{d\eta}{d\xi} = \frac{A\xi(\xi-1)(s-\xi)}{\eta} - B(\xi-c),$$

where

$$A = 3h(\gamma+1),$$

$$B = 3 + 2h,$$

$$c = 3(\gamma+1)(s+1)/4\gamma(3+2h).$$

The required solution is one for which  $\eta$  runs through positive values from zero at  $\xi=1$  to zero at  $\xi=s$ , and  $s$  may have any value from unity to the upper limit  $(\gamma+1)/(\gamma-1)$ . The terminal points  $(1, 0)$  and  $(s, 0)$  are "singular points" at which the value of  $dy/dx$  becomes indeterminate. When the origin is transferred to such a point and terms of the second order are neglected the differential equation assumes in general the form

$$dy/dx = (ax+by)/(a'x+b'y).$$

By putting  $y=mx$  a quadratic equation

$$b'm^2 + (a'-b)m - a = 0$$

is found whose roots determine two special directions at the point. The arrangement of the curves which satisfy the differential equation depends on the nature of the roots of this quadratic\*.

The analysis is a good deal simplified in the present case owing to the special values,  $a'=0$  and  $b'=1$ . We have

$$dx/y = dy/(ax+by) = d(y-mx)/(b-m)y+ax.$$

If  $m$  is a root of  $m^2-bm-a=0$  then  $a=-m(b-m)$ , and  $(b-m)$  is the other root, and so

$$d(y-m_1x)/m_2(y-m_1x) = d(y-m_2x)/m_1(y-m_2x),$$

giving as approximate integral near the origin the equation

$$(y-m_1x)^{m_1} = C(y-m_2x)^{-2}.$$

When the roots  $m_1, m_2$  are real and have the same sign the point is a "node." An infinite number of solution-curves pass through the point, arranged like a family of parabolas having a common tangent which has the special direction of

\* See Picard, *Traité d'Analyse*, iii. p. 206.

smaller slope. When the roots are real with opposite signs the point is a "col." The curves are then like a family of hyperbolas with common asymptotes and two solution-curves only leave the point, one in each of the special directions. When the roots are complex the singular point is a "focus" and the solution-curves wind round it in the manner of a spiral. For purely imaginary roots we have a "centre," the arrangement round it being similar to the case of concentric ellipses.

*Nature of the singular points.*

It is necessary first to settle the character of the terminal points in the present case. When the reductions are effected the quadratics are found to be :

$$\text{at } \xi = 1, \quad m^2 - B(c-1)m - A(s-1) = 0,$$

$$\text{at } \xi = s, \quad m^2 + B(s-c)m + As(s-1) = 0.$$

It is seen at once that the former point is always a "col," but the nature of  $\xi = s$  requires some consideration. This is the more necessary because Lord Rayleigh, in his numerical work, took for the constant  $h$  the value of  $\cdot 4$ , in accordance with Maxwell's law of the inverse fifth power for molecular repulsions. The values given by Meyer and Jeans for actual gases are in the neighbourhood of  $\cdot 6$ . One would like to be assured of the possibility of the wave for any values of the constants  $h$  and  $\gamma$ . If the roots of the second quadratic are real the point is a node, because the constant term is essentially positive. The condition for this is

$$B^2(s-c)^2 - 4As(s-1) > 0,$$

which has to hold for all values of  $s$  from unity to  $(\gamma+1)/(\gamma-1)$ . For  $s=1$  the left-hand side is a complete square, and when the other extreme value is put for  $s$ , and  $B$  and  $A$  replaced by their values, the expression again reduces to a complete square, viz.

$$4(\gamma+1)^2(h-\frac{3}{4})^2(\gamma-1)^2.$$

Therefore the expression is positive for all intermediate values of  $s$ , provided the quadratic in  $s$  has not two real roots lying in the interval.

Written out in full the equation is

$$\{64\gamma^2h^2 - 48(2\gamma^2 - \gamma + 1)\gamma h + 9(3\gamma - 1)^2\} s^2 \\ + 6(\gamma + 1) \{s(2\gamma - 1)\gamma h - 3(3\gamma - 1)\} s + 9(\gamma + 1)^2 = 0.$$

There are three critical values of  $h$  in ascending order of magnitude (when  $\gamma > 1$ ),

$$h_1 = 3(3\gamma - 1)/8\gamma(2\gamma - 1),$$

$$h_2 = 3/4\gamma,$$

$$h_3 = 3\{2\gamma^2 - \gamma + 1 - 2(\gamma - 1)\gamma^{1/2}(\gamma + 1)^{1/2}\}/8\gamma.$$

For  $h = h_1$  the coefficient of  $s$  changes sign,

for  $h = h_2$  the discriminant of the equation vanishes,

for  $h = h_3$  the coefficient of  $s^2$  changes sign.

For  $0 < h < h_1$  the coefficients are  $+ - +$ , roots imaginary,

$$h_1 < h < h_2 \quad \text{,,} \quad \text{,,} \quad + + +, \quad \text{,,} \quad \text{,,}$$

$$h_2 < h < h_3 \quad \text{,,} \quad \text{,,} \quad + + +, \text{ roots real and both negative,}$$

$$h_3 < h \quad \text{,,} \quad \text{,,} \quad - + +, \text{ roots real and of opposite sign.}$$

Therefore in no case do both roots lie in the interval between the extreme values of  $s$ . We conclude that  $\xi = 1$  is always a col and  $\xi = s$  always a node. It remains to show that one of the infinite numbers of solution-curves at  $(s, 0)$  runs, through positive values, to the point  $(1, 0)$ .

### *Geometrical discussion of the equation.*

A general idea as to the configuration in the plane of  $(\xi, \eta)$  of the curves which satisfy the differential equation is obtained by considering the "isoclines" along with the "inflexion-locus." An isocline is the locus of points at which  $d\eta/d\xi$  has an assigned value,  $p$ . The inflexion-locus passes through the points where  $d^2\eta/d\xi^2$  vanishes; on opposite sides of it the solution-curves have their concavities turned in opposite directions. At the intersection of the inflexion-locus with an isocline  $p$ , the isocline itself has the slope  $p^*$ .

In the present case the isoclines are the cubic curves

$$A\xi(\xi - 1)(s - \xi) = \eta\{B(\xi - c) + p\}.$$

They all pass through the three singular points  $\xi = 0, 1, s$  on the  $\xi$ -axis. This axis itself is the isocline  $p = \infty$ ; the solution-curves cross it everywhere at right angles. Special importance attaches to the curve  $p = 0$ ,

$$\eta = A\xi(\xi - 1)(s - \xi)/B(\xi - c).$$

\* See D'Ocagne, *loc. cit.* p. 153.

This has  $\xi=c$  as asymptote. It will be found later that essential differences arise according as this does or does not lie in the section between  $\xi=1$  and  $\xi=s$ .

There are three special values of  $p$  for which the cubic breaks up into a straight line through one of the singular points and a parabola through the other two. These are

$$p = Bc, \quad \xi = 0, \quad \text{and} \quad B\eta = A(\xi-1)(s-\xi);$$

$$p = B(c-1), \quad \xi = 1, \quad \text{and} \quad B\eta = A\xi(s-\xi);$$

$$p = B(c-s), \quad \xi = s, \quad \text{and} \quad B\eta = -A\xi(\xi-1).$$

The equation of the inflexion-locus is

$$B\eta^3 + A\{3\xi^2 - 2(s+1)\xi + s\}\eta^2 - AB(\xi-c)\xi(\xi-1)(s-\xi)\eta \\ + A^2\xi^2(\xi-1)^2(s-\xi)^2 = 0.$$

There is a node at each singular point and the tangents to the two branches of the curve have the "special directions."

In order to examine the disposition of the branches with respect to the tangents it is necessary to take into account terms of the third degree, when the equation is referred to the double point as origin. The terms of second and third degree may be written

$$(y-m_1x)(y-m_2x) = u_3.$$

To find the side of the tangent  $y=m_1x$  on which the curve lies, it is only necessary to consider the sign of

$$y-m_1x = u_3/(y-m_2x) = u_3(m_1x^2)/(m_1-m_2),$$

where  $u_3(m)$  means that the values  $x=1, y=m$  have been inserted in  $u_3$ .

In the present case, when account is taken of the quadratic equation satisfied by  $m, m_2$ , it is found that the expression for  $u_3(m)$  can be written in the forms

$$-B(1-c)m\{Bm+A(2-s)\}/A(s-1) \quad \text{at} \quad \xi=1;$$

$$B(s-c)m\{Bm+A(2s-1)\}/As(s-1) \quad \text{at} \quad \xi=s.$$

Thus at  $\xi=1$  critical values of  $s$  are those which make  $c=1$  or  $m=-A(2-s)/B$ . The former value is given at once by the meaning of the constant  $c$  as

$$s = \{\gamma(9+8h)-3\}/3(\gamma+1) = s_1,$$

say. For  $\gamma=1.41, h=.4, s_1$  is 1.96, and more generally it can be seen that the value lies within the range with which we are concerned.

The other critical value is found by inserting the given value of  $m$  in the quadratic equation which gives the special

directions and solving the equation so obtained for  $s$ . In this case it is found on examination that for the actual range of values of  $\gamma$  and  $h$  the roots do not correspond to values of  $s$  occurring in the question. One root is negative and the other positive but less than unity. Therefore  $s_1$  is the only critical value found at  $\xi=1$ . It has been met with already, as the value for which the asymptote  $\xi=c$ , of the zero isocline, passes within the range, from  $\xi=1$  to  $\xi=s$ , inside which the relevant solutions of the differential equation lie.

At  $\xi=1$  the slopes  $m_1 m_2$  have opposite signs; we are concerned only with the positive value, and the above examination shows that the corresponding branch of the inflexion-locus lies below the tangent for  $s < s_1$  and above for  $s > s_1$ .

Near the other terminal point,  $\xi=s$ , the critical cases are given by  $s=c$  and  $m = -A(2s-1)/B$ .

It is found that the former condition leads to a value of  $s$  which is the reciprocal of that found above for  $c=1$  and which therefore is less than unity and irrelevant. On the other hand, the quadratic for  $s$  got by using the second condition has one root lying in the range of the problem. Its expression in terms of  $\gamma$  and  $h$  is lengthy and need not be written out here. We shall call it  $s_2$ . The value for  $\gamma=1.41$  and  $h=.4$  is 2.24. At this point both the tangents have negative slopes, so that both branches of the inflexion-locus lie in the region  $1 < \xi < s$ ,  $\eta > 0$ , with which we are concerned. For  $s < s_2$  both branches are below the tangents, for  $s > s_2$  the curve lies above the tangent of smaller slope and below that of greater slope. Examples of these different configurations will be seen in the diagrams which follow.

Another point of some importance is the relation to the special directions of the isocline of zero slope, where it passes through the singular points. Its equation is

$$\eta = A\xi(\xi-1)(s-\xi)/B(\xi-c),$$

$$\text{so} \quad d\eta/d\xi = A(s-1)/B(1-c) \quad \text{at } \xi=1,$$

$$\text{and} \quad = -As(s-1)/B(s-c) \quad \text{at } \xi=s.$$

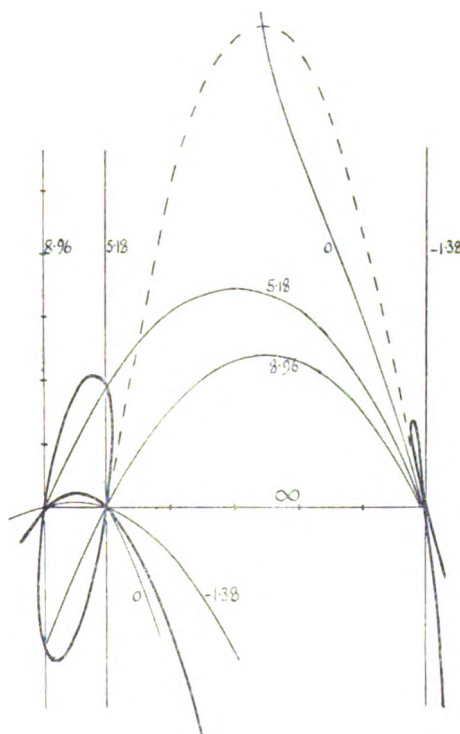
When these values are inserted in the quadratics for  $m$  they make the left-hand side reduce to  $m^2$ . It follows that the zero isocline lies outside the angle formed by the lines  $y=m_1x$ ,  $y=m_2x$  drawn in the direction of positive  $x$ .

#### *Discussion of particular cases.*

Lord Rayleigh evaluated the coefficients of his equation, putting  $\gamma=1.41$ ,  $h=.4$ . This value of  $\gamma$  leads to 5.88 as the maximum  $s$ . By what appears to be an oversight

Lord Rayleigh replaces this by 6, which corresponds to  $\lambda=1.40$ , but the effect of this difference on the numerical values of the coefficients is negligible. It should be noted that there is nothing in the purely mathematical aspect of the question to indicate the existence of this upper limit to  $s$ . It arises physically, from the consideration of the pressure. The formal solution of the differential equation with  $\gamma=1.41$  and  $s=6$  would lead to infinite and negative pressures in the wave.

Fig. 1.



$$S = 6$$

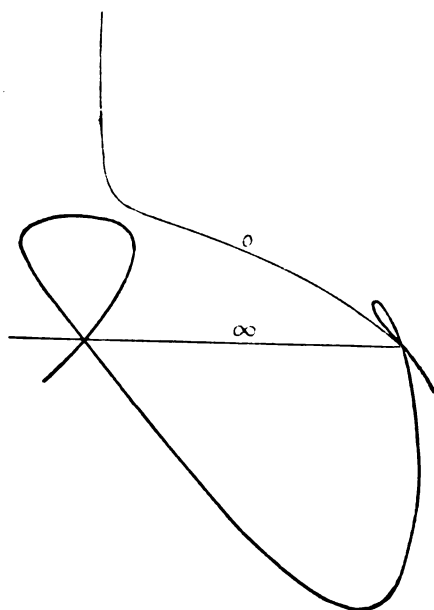
Lord Rayleigh worked his way from point to point by Runge's method, beginning at the col  $\xi = 1$  and starting off along the special direction of positive slope. He found that the path led to the node at  $\xi = 6$ . Evidently this process could not have been applied in the reverse direction.

It is convenient to begin with the extreme case  $s=6$ . The distribution of the loci is shown on fig. 1, which is extended to the origin in order to complete the run of the



curves. The isocline for  $p=0$  is drawn, having its asymptote along  $\xi=c=2.36$ , and also the special isoclines which break up into a straight line and parabola. The inflexion-locus is drawn with a heavier line. It will be noticed that it passes through the intersections of line and parabola on the special isoclines. As already mentioned, the axis is the isocline  $p=\infty$ . The broken curve is the solution of the equation plotted from Lord Rayleigh's numbers. The special directions are the tangents to the inflexion-locus at the singular points.

Fig. 2.



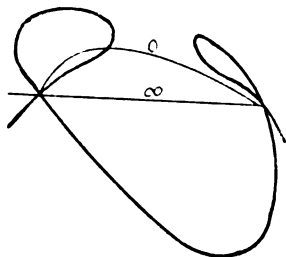
$$S = 2$$

A study of these curves will make evident the existence of the required solution-curve. A family of curves leaves the singular point  $(6, 0)$  all touching the special direction of smaller inclination to the axis and running in a region where  $d^2\eta/d\xi^2$  is negative, *i. e.* the concavity is downwards. Since the locus  $p=0$  makes a still smaller angle with the axis, the curves, in the domain of positive  $\eta$ , encounter the locus and turn downwards before they meet the inflexion-locus, so

one curve of the family passes downward through each point of the axis between  $(1, 0)$  and  $(6, 0)$ , and we reach the required solution-curve as a limit. There is, of course, the same sort of ultimate discontinuity as is found in bringing hyperbolas up to the asymptotes.

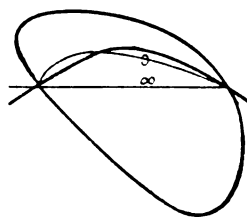
From a physical point of view one would expect that any doubt as to the existence of a solution would attach to the larger values of  $s$ ; this is the opinion expressed by Lord Rayleigh. It is therefore somewhat surprising to find that when the diagram is modified in the way of diminishing  $s$ , the matter becomes not more, but less obvious. Progressive changes in the configuration of the field take place in the manner described below, and may

Fig. 3.



$$S = 1.7$$

Fig. 4.



$$S = 1.6$$

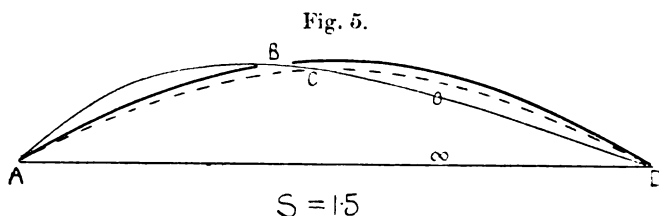
be followed in figs. 1-4, which have been drawn for  $s=6, 2, 1.7, 1.6$ .

It will be enough to consider the zero isocline and the inflexion-locus. When  $s$  becomes less than 1.96 there is no asymptote to  $p=0$  between the terminal points, the curve then runs in an arc from one point to the other.

At  $s=2.24$  and  $s=1.96$  respectively, the inner sides of the loops on the inflexion-locus pass across the tangents, but notwithstanding this, the loops at first persist, the branch of the curve crossing back over the tangent. (See fig. 3 for  $s=1.7$ .) With continued decrease of  $s$  the two loops approach each other, as if by a mutual attraction. For some value between 1.7 and 1.6 they meet, and this is followed by a complete change in the configuration, as shown on fig. 4. In this tangled arrangement of the two loci it is not so easy to follow the course of the solution-curves. We shall use

fig. 5 for  $s=1.5$ , on which the air-wave solution, calculated by Runge's method, has been inserted as a broken line.

Consider the curves which cross  $p=0$  between the singular point A and the highest point B, where it intersects the inflexion-locus. These at first turn upwards until they meet the inflexion-locus where the curvature is reversed, the slope then decreases and becomes zero again at some point on BC,



and thence the curves, remaining concave downwards, run into the node D, between the broken line and the inflexion-locus. On the other hand, the curves which rise perpendicularly from the axis bend over to meet the zero isocline at points between CD and reach the node without encountering the inflexion-locus, filling up the region between the broken line and the zero isocline. The curve required for the wave-solution is the limiting one which separates these two sets.

## II. PROPERTIES OF THE WAVE.

### *Summary of the Physical Theory.*

In the following outline of the argument by which the differential equation is reached the equations are numbered as in Lord Rayleigh's paper. The motion is supposed to be stationary. The velocity of the air is abruptly decreased from the constant value  $u_1$  to the constant  $u_2$  in passing the wave. Conservation of mass gives  $u_1/r_1 = u_2/r_2 = m$  (the "mass-velocity"). By means of this the specific volume  $v$  may be substituted for the velocity  $u$  in the equation of motion. When this is done the integral found is

$$p + m^2 v - \frac{4}{3} m \mu \frac{dv}{dr} = \text{constant}.$$

$$= p_1 + m^2 v_1 = p_2 + m^2 v_2, \quad \dots \quad (87)$$

which enables  $p$ , and also  $\theta$  the absolute temperature, at any point, to be expressed in terms of  $v$ .

If the air in travelling a distance  $dr$  undergoes a small

change of condition specified by  $dp, dv$ , it must have received heat of amount given (in mechanical units) by

$$(\gamma-1)dQ = \gamma p dv + v dp.$$

By use of (87) this can be expressed in terms of  $v$  only. Now  $dQ$  is made up of  $dQ_1$ , heat passing into the unit mass by conduction, and  $dQ_2$ , heat generated by viscosity. The latter part is equal to

$$\frac{4}{3}m\mu\left(\frac{dv}{dx}\right)^2 dx. \quad \dots \quad (92)$$

Subtracting this from the expression for  $dQ$  the remainder is found to be a complete differential and its integration gives for the total heat received by conduction between the initial state  $v_1$  and the value  $v$

$$(\gamma-1)Q_1 = \gamma(p_1 + m^2v_1)v - (\gamma+1)\frac{1}{2}m^2v^2 + \frac{4}{3}m\mu v \frac{dv}{dx} + \text{const.}$$

But the total heat conducted into the gas in passage from the one uniform condition to the other is nil. Expressing this fact we get the important relation

$$(p_1 + m^2v_1) = (p_2 + m^2v_2) = (\gamma+1)m^2(v_1 + v_2)/2\gamma. \quad (86)$$

By means of it the expression for the conducted heat can be put into the form

$$(\gamma-1)Q_1 = \frac{1}{2}(\gamma+1)m^2(v_1 - v)(v - v_2) + \frac{4}{3}m\mu v \frac{dv}{dx}. \quad (96)$$

The last step is to connect  $Q_1$  with the temperature  $\theta = pv/R$  as given by (87) through the equation of conduction in the form

$$mQ_1 = k d\theta/dx. \quad \dots \quad (74)$$

This gives the differential equation required.

#### *Relation between terminal states.*

From eqn. (86), putting  $s$ , as before, for  $v_1/v_2 = \rho_2/\rho_1$ ,

$$p_2/p_1 = \{(\gamma+1)s - (\gamma-1)\} / \{(\gamma+1) - (\gamma-1)s\},$$

$$\theta_2/\theta_1 = \{(\gamma+1)s - (\gamma-1)\} / \{s\{(\gamma+1) - (\gamma-1)s\}\}.$$

The pressure and temperature ratios are infinite for  $s = (\gamma+1)/(\gamma-1)$ . On account of the limited range of  $s$  it is convenient to take it, rather than the pressure-ratio, as the variable defining the amplitude of the wave.

*Rate of propagation.*

The plan of making the wave stationary, although it is adapted to the mathematical investigation of the motion, does not lend itself to a clear physical conception. For this it is better to consider one of the two regions of air as being at rest. There is then a choice between two alternatives. We may think of a wind of high-pressure air moving with velocity  $(u_1 - u_2)$  into a region of low-pressure quiescent air, its front advancing through the latter at rate  $u_1$ . Or we may imagine a moving mass of low-pressure air with velocity  $(u_1 - u_2)$  piling itself up against a block of high-pressure air as it comes to rest, the thickness added per second being  $u_2$ . In either case the process will continue indefinitely only when there is the special adjustment of pressure-ratio to density-ratio given above. We shall adopt the former conception as more like what happens in an explosion-wave, and we shall find the velocity of propagation  $u_1$  in terms of the ordinary velocity of sound in the quiescent low-pressure gas, which will be denoted by  $u_1' = (\gamma p_1 v_1)^{1/2}$ .

Equation (86) gives

$$m^2 = 2\gamma s p_1 / v_1 \{(\gamma + 1) - (\gamma - 1)s\},$$

$$\therefore u_1/u_1' = m_1 v_1 / (\gamma p_1 v_1)^{1/2} = [2s / \{(\gamma + 1) - (\gamma - 1)s\}]^{1/2}$$

$$\text{and } u_2/u_1' = [2/s \{(\gamma + 1) - (\gamma - 1)s\}]^{1/2}.$$

It will be seen that  $u_2$  has a minimum value for

$$s = (\gamma + 1)/2(\gamma - 1)$$

and that both velocities become  $u_1'$  for  $s=1$ .

On fig. 6 the velocities, the pressure-ratio, and the temperature-ratio are plotted against  $s$ , for  $\gamma=1.40$ . For convenience the ratios  $p_1/p_2$ ,  $\theta_1/\theta_2$  less than unity, are taken instead of their reciprocals. The vertical distance between the two velocity-curves gives the wind-velocity in the high-pressure region.

*Variation of  $p v \theta$  within the wave.*

Once  $\eta$  has been determined as a function of  $\xi$  from the differential equation, by an arithmetical or geometrical method, it becomes possible to examine the state of affairs inside the narrow layer of transition which constitutes the wave.

In the first place  $(p, \theta)$  are immediately connected with  $\epsilon$ .

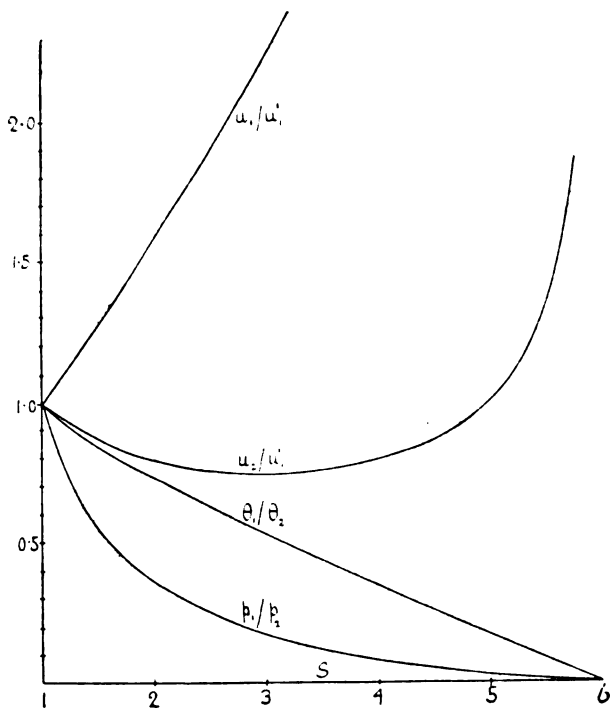
For from equations (86) (87) we obtain

$$p/p_1 = \{(\gamma+1)(s+1)\xi - 2\gamma\xi^2 - \frac{4}{3}\gamma\eta\}/\xi\{(\gamma+1)s - (\gamma-1)\},$$

and  $\theta/\theta_1$  is the same expression multiplied by  $v/v_1$  or  $\xi/s$ . It remains to connect  $v$  or  $\xi$  with distance measured along the direction of propagation. This can be done by mechanical or arithmetical quadrature. By definition

$$dx/d\xi = -2\mu'\xi/\eta.$$

Fig. 6.



The length  $\mu' = \mu/m$  will depend on the temperature at the point and on  $s$ . To get a definite unit,  $\mu'$  must be expressed in terms of  $\mu_1$  the viscosity at temperature  $\theta_1$  and the limiting value of mass-velocity,  $m_1$ , applicable to sound-waves in the initial condition of the gas. The length

$$\mu_1/m_1 = \text{viscosity} / \text{sound-velocity} \times \text{density}$$

has been shown by Lord Rayleigh to be of very small size, of the order  $\frac{1}{3} \times 10^{-5}$  cm. for air under ordinary conditions.

If we write  $\mu/\mu_1 = f(\theta/\theta_1)$  and use the expression already found for  $m$  as a function of  $s$  which gives

$$m/m_1 = [2s/\{(\gamma+1) - (\gamma-1)s\}]^{1/2},$$

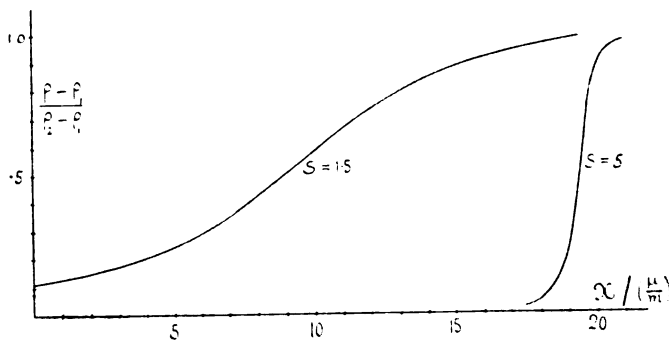
we have

$$dx/d\xi = -2f(\theta/\theta_1) \cdot [\{(\gamma+1) - (\gamma-1)s\}/2s]^{1/2} \cdot (\xi/\eta) \cdot (\mu_1/m_1).$$

The expression on the right can be plotted against  $\xi$ , and the integral curve then gives us the power to associate each value of  $\xi$  with a value of  $x$ , in terms of the length-unit  $\mu_1/m_1$ . The origin of  $x$  is of course arbitrary.

This work has been carried out for the two cases  $s=1.5$  and  $s=5$ ,  $\gamma=1.41$ . Runge's process was used to find  $\eta$  for values of  $\xi$  at intervals of .02 and .2 respectively. The

Fig. 7.

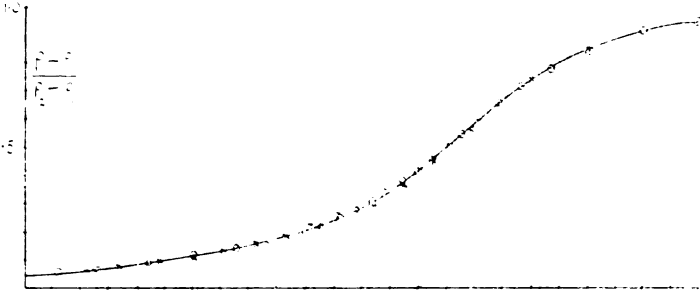


theoretical law for variation of viscosity was taken, by which  $f(\theta/\theta_1) = (\theta/\theta_1)^{1/2}$ . A Coradi Integrator was used. The results are shown on fig. 7. In order to compare the two cases the quantity plotted is the fractional rise in density  $(\rho - \rho_1)/(\rho_2 - \rho_1)$ . It will be seen that the larger increase of density takes place in a much shorter distance. The difference is still more marked when one considers the time rather than the distance, because the five-fold condensation-wave travels at about four times the speed of the other.

It is interesting to notice that the difference between the two graphs is purely one of horizontal scale. By multiplying the abscissae of the curve for  $s=5$  by 11 it can be brought into coincidence with the other. This is shown on fig. 8, where the calculated points for  $s=5$  and  $s=1.5$  are marked with a circle and cross respectively.

It does not seem worth while to reproduce the curves for the pressure, which are of the same general character as these. In connexion with the temperature, however, a point of some physical interest arises.

Fig. 8.



#### *Analysis of the temperature-rise.*

There are three different causes which bring about the heating of the gas:—

- (1) The adiabatic compression, which alone is operative on the ordinary theory of sound.
- (2) Conduction: the gas at first gains heat from warmer parts and then loses an equal amount to colder parts.
- (3) Viscosity.

The question of the relative importance of these three factors naturally suggests itself. It can be answered by carrying the analysis of Lord Rayleigh a little farther, if we assume the specific heat  $c$  to be independent of the temperature. Denote by  $\theta_a$ ,  $\theta_c$ ,  $\theta_v$  the temperatures which would be produced by the action of the three causes separately so that the actual rise  $(\theta - \theta_1)$  at a point is the sum of  $(\theta_a - \theta_1)$ ,  $(\theta_c - \theta_1)$ ,  $(\theta_v - \theta_1)$ .

The formulæ already given furnish  $(\theta - \theta_1)$  and  $(\rho_c - \theta_1)$ . The adiabatic heating is known, and so all three contributions can be separated.

We have

$$\theta_c - \theta_1 = Q_1/c = (\gamma - 1)Q_1/R = (\gamma - 1)Q_1\theta_1/\rho_1 r_1,$$



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which gives, by use of (96) and the expression for  $m^2$ ,

$$\frac{(\theta_c - \theta_1)}{\theta_1} = \gamma \{ (\gamma + 1)(s - \xi)(\xi - 1) - \frac{4}{3}\eta \} / s \{ (\gamma + 1) - (\gamma - 1)s \},$$

while

$$\theta/\theta_1 = \{ (\gamma + 1)(s + 1)\xi - 2\gamma\xi^2 - \frac{4}{3}\gamma\eta \} / s \{ (\gamma + 1) - (\gamma - 1)s \} :$$

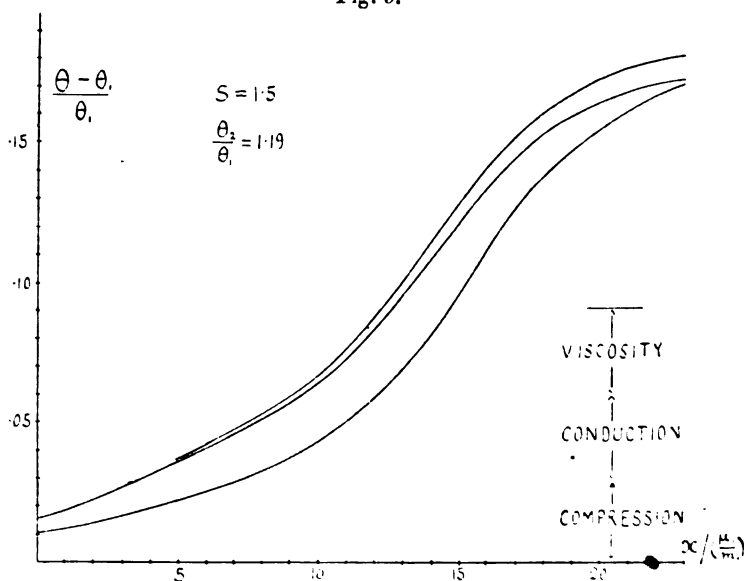
on subtraction the term in  $\eta$  disappears, and we obtain

$$\frac{(\theta - \theta_c)}{\theta_1} = \frac{(\gamma - 1) \{ \gamma\xi^3 - (\gamma + 1)(s + 1)\xi + (\gamma + 1)s + s^2 \}}{s \{ (\gamma + 1) - (\gamma - 1)s \}}$$

This expression combines the temperature-increases due to compression and viscosity. The former of these is given by

$$\theta_a/\theta_1 = (v_1/v)\gamma^{-1} = (s/\xi)\gamma^{-1}.$$

Fig. 9.

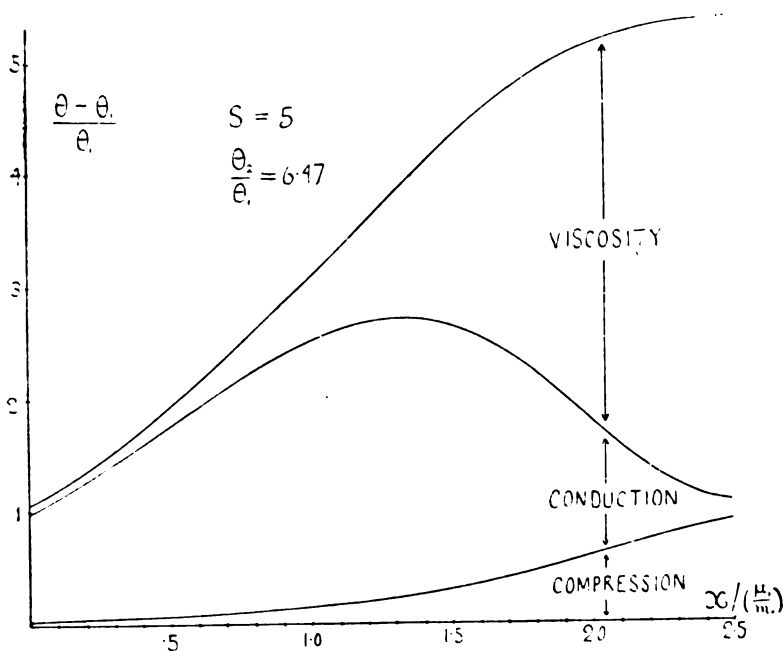


Thus the adiabatic and the viscosity effects separately are found to be functions purely of the density at the point.

The calculations have been carried out for the two cases  $s=1.5$  and  $s=5$ , and the results are displayed on figs. 9 and 10. The horizontal scale of distance is opened up tenfold in the latter diagram.

The ordinate of the highest curve gives the actual temperature and the three segments into which it is divided by the other curves show how the total rise of temperature is made up, the order upwards being the adiabatic, conductivity, and

Fig. 10.



viscosity parts. The central segment disappears at the limits of the wave. The diagrams present a striking contrast. For the wave of small amplitude the greater part of the heating is due to the adiabatic compression. This was to be expected: but it is rather remarkable how with a high degree of compression the relation is reversed. The greater part of the permanent heating is then due to the action of viscosity.

LXXXV. *Stability of the Atom.* By Prof. D. N. MALLIK, B.A., Sc.D., F.R.S.E., Muslim University, Aligarh, India\*.

*Summary.*

LARMOR has shown that in a permanently stable system of "electrons" (*e.g.* a system of electrons and a nucleus forming an atom) the vector sum  $|e\dot{r}|$  is constantly zero, the radiation of energy per unit time being  $\frac{2}{3} \frac{e^2 \dot{r}^2}{c}$ , where  $\dot{r}$  is the acceleration of an electron and  $c$  the velocity of light. These expressions are shown to be also deducible by direct integration of the field equation of the electron theory and to be alone consistent with the electron theory of dispersion. The principle of [permanent] stability thus established is proved then (on certain assumptions) to be the necessary consequence of the quantum conditions postulated by Sommerfeld in the case of a [Bohr] atom of Hydrogen.

It is thus shown that the non-emission of radiation by a Bohr atom of Hydrogen and the usual quantum conditions as well as the proper choice of coordinates are all consistent with the classical theory interpreted in terms of quantum ideas. A tentative attempt is then made to extend the theory to more complex atoms.

STABILITY OF THE ATOM.

1. In the usual presentation of Bohr's theory of spectral series it is stated that in the stationary states no radiation is assumed to take place from the atoms themselves in contradistinction to the classical electromagnetic theory or ordinary electrodynamics.

It should be observed, however, that in all cases of dynamical stability of a permanent type, there should not be any such radiation, and accordingly any theory that is to be consistent with the principle of conservation of energy must proceed on postulates suitable for the purpose. The principle that in a permanent dynamical system there should not be any radiation of energy was, in fact, clearly stated by Larmor, who was probably the first to investigate the mechanism of molecular radiation. For he says ('*Æther and Matter*, p. 225):—

"It thus appears that when the orbital motions in a molecule are so constituted that the vector sum  $|e\dot{r}|$  of the

\* Communicated by the Author.

accelerations of all the electrons (*i. e.* positive and negative charges) with due regard to their signs is constantly null, there will be no radiation or very little abstracted from it, and therefore this steady motion will be permanent. The condition that is thus necessary for absence of dissipation by radiation limits the number of types of motions otherwise steady in the molecules that can be permanent."

3. In order to analyse this statement further we may seek, in the first place, to derive the conditions specified above on the general electron theory and then see if this can be made to fit in with Bohr's theory.

4. We have, if  $(\alpha, \beta, \gamma)$  be the magnetic force,

$$\dot{\alpha} = -4\pi c^2 \left( \frac{\partial h}{\partial y} - \frac{\partial g}{\partial z} \right),$$

where  $4\pi(j + \dot{A}) = \left( \frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z} \right),$

A, B, C being the electric moment of electric charges due to a distribution of electrons of volume density  $\rho$

$$= -\rho \{ (x-x_0), (y-y_0), (z-z_0) \} \quad \text{per unit volume,}$$

and  $\frac{\partial A}{\partial x} + \frac{\partial B}{\partial y} + \frac{\partial C}{\partial z} = -\rho = -\left( \frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} \right).$

Hence we have

$$\ddot{\alpha} = c^2 \left[ \nabla^2 \alpha - \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial x} + \frac{\partial \beta}{\partial y} + \frac{\partial \gamma}{\partial z} \right) + 4\pi \left( \frac{\partial \rho z}{\partial y} - \frac{\partial \rho y}{\partial x} \right) \right].$$

If  $\frac{\partial z}{\partial x} + \frac{\partial \beta}{\partial y} + \frac{\partial \gamma}{\partial z} = 0$

$$(\text{magnetic permeability} = 1),$$

we have

$$\ddot{\alpha} = c^2 \left( \nabla^2 \alpha + 4\pi \left( \frac{\partial \dot{C}}{\partial y} - \frac{\partial \dot{B}}{\partial z} \right) \right).$$

This gives

$$\alpha = \frac{4\pi c^2}{D^2 - c^2 \nabla^2} \left( \frac{\partial \dot{C}}{\partial y} - \frac{\partial \dot{B}}{\partial z} \right), \quad \text{where } D \equiv \frac{d}{dt},$$

$$= \frac{4\pi c^2}{2D} \left[ \frac{1}{D + c\nabla} + \frac{1}{D - c\nabla} \right] \left( \frac{\partial \dot{C}}{\partial y} - \frac{\partial \dot{B}}{\partial z} \right),$$

$$= \left( n \frac{\partial}{\partial y} - m \frac{\partial}{\partial z} \right) \frac{4\pi c^2}{2D} \left[ \frac{1}{D + c\nabla} + \frac{1}{D - c\nabla} \right] F(t),$$

$$\text{where } \dot{A}, \dot{B}, \dot{C} = (l, m, n) F(t).$$

But

$$\begin{aligned}
 & \frac{1}{2D} \left\{ \frac{1}{D+c\nabla} + \frac{1}{D-c\nabla} \right\} F(t) \\
 &= \frac{1}{2D} \left[ e^{-ct\nabla} \int e^{ct'\nabla} F(t') dt' + e^{ct\nabla} \int e^{-ct'\nabla} F(t') dt' \right] \\
 &= \frac{1}{D} \int [\cosh c(t-t')\nabla] F(t) dt \\
 &= \frac{1}{4\pi c^2} \int \frac{F\left(t-\frac{r}{c}\right)}{r} d\tau,
 \end{aligned}$$

since  $c(t-t')=r$ , if  $d\tau$ =element of volume.

[Rayleigh's 'Sound,' vol. ii. ch. xiv.]

$$\begin{aligned}
 \therefore \alpha &= \left( n \frac{\partial}{\partial y} - m \frac{\partial}{\partial z} \right) \int \frac{F\left(t-\frac{r}{c}\right)}{r} d\tau \\
 &= \left( n \frac{\partial}{\partial y} - m \frac{\partial}{\partial z} \right) \frac{\phi\left(t-\frac{r}{c}\right)}{r},
 \end{aligned}$$

where  $er = \phi(t)$ .

$$= e(\dot{x}, \dot{y}, \dot{z}).$$

Therefore, if  $H=(\alpha\beta, \gamma)$  and  $\theta$  the inclination of  $r$  to the direction of electronic motion,

$$\begin{aligned}
 H &= \sin \theta \frac{\partial}{\partial r} \left( \frac{er}{r} \right), \\
 &\text{where } \bar{er} \text{ is the value of } er \text{ at } t-\frac{r}{c}, \\
 &= -\sin \theta \left( \frac{er}{r^2} + \frac{e\dot{r}}{cr} \right)_{t-\frac{r}{c}}.
 \end{aligned}$$

5. Again, if the electric force is

$$(X, Y, Z) = 4\pi c^2(f, g, h),$$

where

$$\begin{aligned}
 \ddot{f} + \frac{d}{dt}(\rho\dot{f}) &= V^2 \nabla^2(f+A) \\
 &= c^2 \nabla^2 f
 \end{aligned}$$

( $V$  = velocity in any medium),

we have

$$\ddot{X} = c^2 \nabla^2 X - 4\pi c^2 \frac{d}{dt}(\rho\dot{X});$$

whence

$$X = \frac{1}{2D} \left[ \frac{1}{D - c\nabla} + \frac{1}{D + c\nabla} \right] \left\{ -4\pi e^2 \frac{d}{dt} (\rho \dot{\mathbf{r}}) \right\},$$

i. e.  $X, Y, Z = -(l, m, n) \left( \frac{e \dot{\mathbf{r}}}{r} \right)_{t - \frac{r}{c}}$

[writing  $l, m, n = \frac{d}{dt} (\rho \dot{\mathbf{r}})$  and proceeding as in (4)].

6. Hence, for an isolated electron, the radiation of energy, in accordance with Poynting's theorem,

$$\begin{aligned} &= \frac{1}{4\pi} \int \frac{e^2 \dot{\mathbf{r}}^2}{r^2 c} \sin^2 \theta dS \quad \text{over an infinite sphere} \\ &= \frac{2}{3} \cdot \frac{e^2 \dot{\mathbf{r}}^2}{c}. \end{aligned}$$

Now the quantum condition for radiation of frequency  $\nu$  is

$$W - W' = \nu h,$$

where  $W$  is the total energy,

which in this case becomes (in accordance with quantum ideas)

$$\frac{2}{3} \cdot \frac{e^2 \dot{\mathbf{r}}^2}{c} \Delta t = \frac{1}{3} \frac{e^2}{c} \dot{\mathbf{r}} \Delta v.$$

If the change in the potential energy of the electron is  $\Delta V$ ,

$$\begin{aligned} W - W' &= \frac{1}{2} \Delta m v^2 + \Delta V \\ &= \frac{1}{3} \frac{e^2}{c} \dot{\mathbf{r}} \Delta v = \nu h. \end{aligned}$$

7. These conditions can evidently be satisfied on a suitable postulate as to the operation of the *field*, although for such an [isolated] electron, the equation

$$\frac{1}{2} \Delta m v^2 = \nu h,$$

cannot be satisfied as has been pointed out by Jeans [Eighth Guthrie Lecture], so that if this were the only allowable equation, we should have to admit that an isolated electron cannot emit or absorb radiation.

8. Now the electromagnetic energy expresses the energy residing in the field, so that the fact that the total energy is made up of the energy of electronic system (including the case of an isolated electron) and the field is also clearly

brought out by the equation of art. 6. For the latter is included in V.

9. On this postulate by the application of Lagrange's theorem I have, in a recent paper\*, obtained the equations of an electronic system which are sufficient to explain dispersion and aberration. They also lead to the expression for Lorentz transformations.

10. In the case of a system of electrons forming a permanently stable configuration we must have, in accordance with the above, the vector sum  $\sum \mathbf{e}\dot{\mathbf{r}} = 0$ . This must then refer to the stationary states of Bohr's atom.

Now this condition is the same as

$$\frac{\int \ddot{\mathbf{A}} d\tau}{\int d\tau} = 0, \quad \text{i. e. the mean value of } \ddot{\mathbf{A}} = 0,$$

but since it can be shown that the A's satisfy (for radiation) equations of the form

$$\ddot{\mathbf{A}} + p_0 \mathbf{A} = a_0 \mathbf{f},$$

neglecting terms depending on the induced magnetic field,

$$\text{and} \quad \ddot{\mathbf{f}} + \ddot{\mathbf{A}} = V^2 \nabla^2 (\mathbf{f} + \mathbf{A}),$$

where the quantities have their mean values over a specified region, (say) the volume of an atom, we easily find that no radiation will result if  $(\ddot{\mathbf{A}}, \ddot{\mathbf{B}}, \ddot{\mathbf{C}}) = 0$ .

11. We notice, incidentally, that this gives

$$\nabla^2 (f_0 g_0 h_0) = 0, \quad \text{where } f_0 = (\mathbf{f} + \mathbf{A}), \text{ etc.,}$$

which correlates to the usual equations of equilibrium of an elastic solid, viz.,

$$\nabla^2 (\omega_x, \omega_y, \omega_z) = 0,$$

so that

$$(f_0, g_0, h_0) \propto (\omega_x, \omega_y, \omega_z),$$

where  $\omega_x, \omega_y, \omega_z$  may be defined as rotational strains of the medium or field, as in Macculagh-Larmor theory of the æther or the steady rotation of a corpuscle about the nucleus or about the common centre of gravity of the nucleus and the corpuscles of the Bohr-Rutherford atom in a permanently stable configuration.

12. In order to examine whether this condition for a permanently stable configuration is implied in the Bohr-Sommerfeld theory, it would be useful to recall that this

\* "Electron Theory of Aberration and Lorentz Transformations," Phil. Mag. Sept. 1924.

theory postulates, if account is taken of the motion of the nucleus, the two quantum conditions

$$\int_0^{2\pi} (mr^2 \dot{\phi} d\phi + MR^2 \dot{\phi} d\phi) = nh \quad . \quad . \quad (1)$$

$$\text{and} \quad \int_0^{2\pi} (m\dot{r} dr + M\dot{R} dR) = n'h, \quad . \quad . \quad . \quad (2)$$

where  $m$  = mass of the electron,  
 $M$  = mass of the nucleus,  
 $r$  = distance of an electron from the common C.G.  
 $R$  = distance of the nucleus from the same point,  
 $\phi$  = vectorial angle.

From (1) and (2), we have

$$\begin{aligned} (n + n')h &= \int (mr^2 + MR^2) \dot{\phi} d\phi + \int (m\dot{r} dr + M\dot{R} dR) \\ &= \int (m\dot{x} dx + M\dot{X} dX) + \int (m\dot{y} dy + M\dot{Y} dY) \end{aligned}$$

in cartesianes.

Now writing

$$\frac{r}{m} = \frac{R}{M} = \frac{\rho}{m + M} \equiv \frac{\rho}{\mu},$$

we have

$$\int (mr^2 + MR^2) \dot{\phi} d\phi = \int \mu \rho^2 \dot{\phi} d\phi = 2\pi p$$

$$\text{if } \mu \rho^2 \dot{\phi} = p = \text{const. (for a central orbit)}; \quad . \quad . \quad . \quad (3)$$

similarly,

$$\int (m\dot{r} dr + M\dot{R} dR) = \int \mu \dot{\rho} d\rho,$$

the equation of the relative orbit being

$$\frac{l_0}{\rho} = 1 + \epsilon \cos \phi,$$

where  $\epsilon$  is the eccentricity of the orbit, and  $l_0$  the semi-latus rectum. We have, accordingly,

$$\begin{aligned} (n + n')h &= 2\pi p + \epsilon^2 p \int_0^{2\pi} \frac{\sin^2 \phi}{(1 + \epsilon \cos \phi)^2} d\phi \\ &= \frac{2\pi p}{\sqrt{1 - \epsilon^2}}. \quad . \quad . \quad . \quad . \quad . \quad (4) \end{aligned}$$

Hence we conclude that quantum conditions are necessarily satisfied for all central [relative] orbits.



Moreover,

$$\begin{aligned} \frac{2\pi l'}{\sqrt{1-\epsilon^2}} &= \int (m\dot{x} dx + M\dot{X} dX) + \int (m\dot{y} dy + M\dot{Y} dY) \\ &= m \int (\ddot{x} + \ddot{X}) dx + m \int (\ddot{y} + \ddot{Y}) dy, \end{aligned}$$

if  $m\dot{x} = M\dot{X}$ , etc.

Differentiating this expression with regard to time, on the supposition that the orbit remains unchanged, we have, since

$$\begin{aligned} &\frac{D}{Dt} \int (\xi dx + \eta dy + \zeta dz) \\ &= \int \left( \frac{D\xi}{Dt} dx + \frac{D\eta}{Dt} dy + \frac{D\zeta}{Dt} dz \right) + \int (\xi d\xi + \eta d\eta + \zeta d\zeta) \\ &= \int \left( \frac{D\xi}{Dt} dx + \frac{D\eta}{Dt} dy + \frac{D\zeta}{Dt} dz \right) \text{ for a closed orbit,} \end{aligned}$$

where

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \xi \frac{\partial}{\partial x} + \eta \frac{\partial}{\partial y} + \zeta \frac{\partial}{\partial z}$$

and

$$\xi = \frac{D}{Dt} (x + X) \equiv (\dot{x} + \dot{X})$$

(assuming \* this operation permissible in this case),

$$0 = \int m(\ddot{x} + \ddot{X}) dx + \int m(\ddot{y} + \ddot{Y}) dy,$$

so that

$$\int m \left[ (\ddot{x} + \ddot{X}) \frac{dx}{ds} + (\ddot{y} + \ddot{Y}) \frac{dy}{ds} \right] ds = 0,$$

$$m \int \left[ (\ddot{x} + \ddot{X}) \frac{dx}{dn} + (\ddot{y} + \ddot{Y}) \frac{dy}{dn} \right] dn = 0$$

( $ds$ , an element of arc, and  $dn$ , an element of normal).

Accordingly, since the coefficients of  $ds$  and  $dn$  must have the same sign throughout,

$$\ddot{v} + \ddot{V} = 0,$$

where  $\ddot{v}$  and  $\ddot{V}$  are the resultant accelerations of the electron and the nucleus respectively.

Thus, so long as we are confined to the Bohr orbit of the hydrogen atom, Larmor's condition  $jev = 0$  is satisfied.

13. Incidentally we observe that from (1), (2), and (4)

\* This assumption is involved in Lorentz's theory, see art. 333, Poincaré's 'Electricité et Optique.'

we readily get the expression for the total energy ( $W$ ) as required by theory.

For from the property of the elliptic orbit, we have

$$u^2 = \frac{Ee}{\mu} \left( \frac{2}{\rho} - \frac{1}{a} \right), \quad \dots \dots \dots (5)$$

where  $u$  is the velocity in the orbit, and  $a$  the semi-major axis; also

$$\sqrt{\frac{Ee}{\mu}} l_0 = \frac{p}{\mu}, \text{ from (3),}$$

$$\text{or } \frac{1}{a} = \frac{\mu Ee}{h^2} \cdot \frac{4\pi^2}{(n+n')^2}, \quad \dots \dots \dots (6)$$

which gives, remembering that

$$W = \frac{1}{2}\mu u^2 - \frac{Ee}{\rho} = -\frac{Ee}{2a}, \text{ from (5),}$$

$$W = -\frac{\mu(Ee)^2}{h^2} \cdot \frac{2\pi^2}{(n+n')^2}, \text{ from (6),}$$

where  $E$  is the charge of the nucleus.

14. The quantum conditions of art. 12 are postulates of Bohr's theory which thus seem to be capable of generalization, based on the present analysis.

For since in the case of the hydrogen atom we have  $e[\dot{v} + \dot{V}] = 0$ , we have in *any closed orbit*,

$$\int (\ddot{x} + \ddot{X}) dx + \int (\ddot{y} + \ddot{Y}) dy = 0.$$

Integrating for an interval  $\Delta t$  in accordance with quantum ideas, we should have

$$\left[ \int (\dot{x} + \dot{X}) dx + (\dot{y} + \dot{Y}) dy \right]_2^1 = (N_1 - N_2)h, \text{ say,}$$

the integrations referring to two stationary orbits spanned in the interval  $\Delta t$ , *i. e.*

$$\left[ \int m(\dot{x} + \dot{X}) dx + \int m(\dot{y} + \dot{Y}) dy \right] = N_1 h,$$

for a particular stationary orbit (1);

$$\text{or } \int (m\dot{x} dx + M\dot{X} dX) + \int (m\dot{y} dy + M\dot{Y} dY) = N_1 h,$$

$$\text{i. e. } \int (mr^2 + MR^2)\dot{\phi} d\phi + \int ((m\dot{r} dr + M\dot{R} dR)) = N_1 h.$$

If the orbit is central the first is a *constant*  $= 2\pi p$ , say, which can be written  $= nh$ , in accordance with quantum ideas.

It follows accordingly (as in art. 12) that

$$\int (m\dot{r} dr + M\dot{R} dR)$$

is a *constant* and can be written on the same principle  $= n'h$ , so that  $N_1 = n + n'$ .

15. One of Sommerfeld's reasons for taking  $r, \phi$  as the variables is in one sense a purely analytical one: these coordinates allow the variables in the Hamilton-Jacobi differential equation of motion to be separated. He, however, also suggests a dynamical explanation, which may be generalized as follows:

The general quantum condition deduced from Larmor's condition being

$$\int (m\dot{x} dx + M\dot{X} dX) + \int (m\dot{y} dy + M\dot{Y} dY) = Nh,$$

if we write  $N = n + n'$

and find two variables such that

$$\begin{aligned} \int F(\phi) d\phi + F(\psi) d\psi \\ = \int (m\dot{x} dx + M\dot{X} dX) + \int m\dot{y} dy + M\dot{Y} dY = (n + n')h, \end{aligned}$$

then, if on dynamical grounds we can prove that

$$\int F(\phi) d\phi = \text{const.} = nh \text{ (say),}$$

it follows that

$$\int f(\psi) d\psi = n'h.$$

16. In three dimensions,

$$(x, y, z, X, Y, Z, r, \theta, \phi, R, \theta, \phi)$$

for the hydrogen atom, we have

$$\begin{aligned} \int (m\dot{x} dx + M\dot{X} dX) + \int (m\dot{y} dy + M\dot{Y} dY) + \int (m\dot{z} dz + M\dot{Z} dZ) \\ = \int m(\dot{x} + \dot{X}) dx + \int m(\dot{y} + \dot{Y}) dy + \int m(\dot{z} + \dot{Z}) dz \\ = \int (m\dot{r} dr + M\dot{R} dR) + \int (mr^2 + MR^2)\dot{\theta} d\theta \\ + \int (mr^2 + MR^2) \sin^2 \theta \dot{\phi} d\phi \\ = \int \mu \dot{\rho} d\rho + \int \mu \rho^2 \dot{\theta} d\theta + \int \mu \rho^2 \sin^2 \theta \dot{\phi} d\phi = Nh, \end{aligned}$$

since  $(\ddot{x} + \ddot{X}, \ddot{y} + \ddot{Y}, \ddot{z} + \ddot{Z}) = 0$ , for permanent stability. Again,

$$\mu \rho^2 \dot{\theta} = p = \text{const.}$$

if the force is radial.

Let

$$\int \mu \rho^2 \dot{\theta} d\theta = n_1 h,$$

similarly

$$\mu \rho^2 \sin^2 \theta \dot{\phi} = p' = \text{const.}$$

$$\therefore \int \mu \rho^2 \sin^2 \theta \dot{\phi} d\phi = n_2 h = 2\pi p'.$$

Accordingly (as in art. 12)

$$\int \mu \dot{\rho} d\rho = nh, \quad [N = n + n_1 + n_2].$$

We have thus the *spatial* quantum conditions of Sommerfeld [p. 242, etc. 'Atomic Structure and Spectral Lines'].

These quantum conditions evidently impose a limitation on the inclination of the orbit of the electron to the invariable plane, conditioned by an external field which, however, must be such that the orbit is still practically central.

17. When we proceed to apply the theory to more complex atoms, we are confronted with serious difficulties arising from the fact that the nature of the configuration cannot be worked out in any of these cases on dynamical considerations.

We have, in fact, when there are  $N$  electrons and the nucleus,

$$\begin{aligned} & \int (m \sum_N \dot{r}_s dr_s + M \dot{R} dR) + \int (m \sum_N r_s^2 \dot{\phi}_s d\phi_s + MR^2 \dot{\psi} d\psi) \\ &= \int (m \sum_N \dot{x}_s dx_s + M \dot{X} dX) + \int (m \sum_N \dot{y}_s dy_s + M \dot{Y} dY), \end{aligned}$$

where  $x_s, y_s, r_s, \phi_s$  define the position of the  $s$ th electron, and  $X, Y, R, \psi$  that of the nucleus, according to the scheme

$$\sum m x = MX,$$

$$\sum m y = MY.$$

Now

$$\int [m \sum_N r_s^2 \dot{\phi}_s d\phi_s + MR^2 \dot{\psi} d\psi] = \text{const.} = nh$$

in accordance with quantum ideas, if the orbits are central, so that

$$\begin{aligned} & \int (m \sum_N \dot{r}_s dr_s + M \dot{R} dR) + nh \\ &= \int m \sum_N (\dot{x}_s + \dot{X}) dx_s + \int m \sum_N (\dot{y}_s + \dot{Y}) dy_s. \end{aligned}$$

18. The conditions of permanent stability, however, are

$$\sum \ddot{x}_s + \ddot{X} = 0, \quad \sum \ddot{y}_s + \ddot{Y} = 0.$$

for this gives vector sum

$$| \sum e \vec{r}_s + E \vec{V} | = 0.$$

These conditions may be satisfied if we postulate

$$\int (m \dot{r}_s dr_s + M \dot{R} dR) = n'h \quad (\text{say})$$

$$\text{and} \quad dx_1 = dx_2 = \dots, \quad dy_1 = dy_2 = \dots$$

as equations of constraints ;

$$\text{i. e.} \quad \ddot{x}_s + \ddot{X} = 0, \quad \ddot{y}_s + \ddot{Y} = 0 \quad (\text{each term separately}).$$

In this event, it is reasonable to suppose that the quantum condition will split up into

$$\int (m \dot{r}_s dr_s + \frac{M}{N} \dot{R} dR) = n_s'h, \text{ etc.}$$

This, of course, will involve the supposition that there is no interaction between the electrons themselves and that each electron, together with the corresponding portion of the nucleus, behaves like a hydrogen atom. This is probably approximately true for the neutral helium atom.

19. Or, we may have the electrons arranged in groups ; for each group we should have  $dx_1 = \dots = dx_s$ , and a quantum condition of the type

$$\int \sum_p m \dot{r}_s dr_s + \frac{Mp}{N} \dot{R} dR = n_p'h$$

(for a group of  $p$  electrons).

Separation of these groups according to the nature of the bonds between them and the nucleus as well as the magnitude of the interaction between the electrons will require further consideration.

20. For a number of electrons in three dimensions, we have (with obvious notation)

$$\begin{aligned} & \int (\sum m \dot{x}_r dx_r + M \dot{X} dX) + \dots + \dots \\ &= \int \sum m (\dot{x}_r + \dot{X}) dx_r + \dots + \dots \\ &= \int m \sum (\dot{r}_s dr_s + r_s^2 \dot{\phi}_s \delta \phi_s + r_s^2 \sin^2 \phi_s \dot{\psi}_s \delta \psi_s) \\ & \quad + \int M (\dot{R} dR + R^2 \dot{\chi} d\chi + R^2 \sin^2 \chi \dot{\theta} d\theta). \end{aligned}$$

The condition for permanent stability will be satisfied if  $(\ddot{x}_r + \ddot{X}, \ddot{y}_r + \ddot{Y}, \ddot{z}_r + \ddot{Z}) = 0$ , separately or in groups. Accordingly either of these expressions is constant  $= Nh$ , say, if the orbits are still central. But for a central orbit

$$\int (\sum m r_s^2 \dot{\phi}_s^2 \delta \phi_s + M R^2 \dot{\chi} d\chi) = \text{const.} = n_1 h, \text{ say,}$$

and

$$2\pi [\Sigma m r_s^2 \sin^2 \phi_s \dot{\psi}_s + MR^2 \sin^2 \chi \dot{\theta}] = \text{const.} = n_2 h, \text{ say ;}$$

$$\therefore \int (m \Sigma \dot{r}_s dr_s + MR dR) = \text{const.} = n_3 h,$$

so that

$$N = n_1 + n_2 + n_3,$$

where  $n_1, n_2, n_3$  may each split up into a number of quantum numbers.

In fact, if the independent coordinates defining the system are  $p_1, p_2, \dots, p_r, \dots$ , there will be quantum conditions of the type

$$\int \left[ m \Sigma (\dot{x}_r + \dot{X}) \frac{\partial x_r}{\partial p_1} + \dots + \dots \right] dp_1 = n_{p_1} h, \text{ etc.}$$

This is of immediate application to the model of Helium atom as conceived by Landé and Bohr, and will be dealt with in a future paper.

21. Again, if  $2T$  = kinetic energy of the system,

$$2T = \Sigma m (\dot{x}_r^2 + \dot{y}_r^2 + \dot{z}_r^2) + M (\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2);$$

but since  $\Sigma m \dot{x}_r = M \dot{X}$ ,

$$2T = m \{ \Sigma (\dot{x}_r + \dot{X}) \dot{x}_r + \Sigma (\dot{y}_r + \dot{Y}) \dot{y}_r + \Sigma (\dot{z}_r + \dot{Z}) \dot{z}_r \}.$$

$$\therefore \frac{\partial T}{\partial \dot{p}_r} = m \left\{ \Sigma (\dot{x}_r + \dot{X}) \frac{\partial \dot{x}_r}{\partial \dot{p}_r} + \dots + \dots \right\}.$$

Now

$$\frac{\partial \dot{x}_r}{\partial \dot{p}_r} = \frac{\partial x_r}{\partial p_r};$$

$$\therefore \frac{\partial T}{\partial \dot{p}_r} = m \left\{ \Sigma (\dot{x}_r + \dot{X}) \frac{\partial x_r}{\partial p_r} + \dots + \dots \right\}.$$

Thus the quantum conditions postulated are of the type

$$\int \frac{\partial T}{\partial \dot{p}_r} dp_r = n_{p_r} h,$$

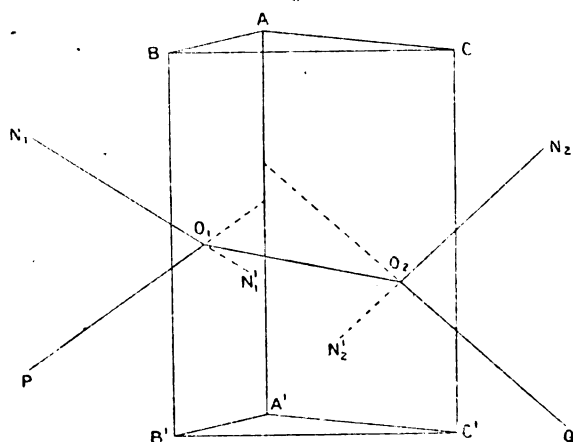
which may be shown to satisfy Larmor's conditions for permanent stability on a proper choice of constraints which must for the present be a matter of speculation.

A proof of this theorem, as well as several other postulates of quantum theory, will be given in a paper on "The Postulates of the Quantum Theory" which is ready for publication.

LXXXVI. *Curvature of the Spectral Lines in a Prism Spectroscope.* By G. SUBRAHMANYAM, M.A., and D. GUNNIAYA, M.A.\*

IT is a matter of common observation that the spectral lines obtained with a prism spectroscope are curved with their convex sides turned towards the red end of the spectrum. This, no doubt, forms an important difference between the dispersion spectra and the diffraction spectra. Excepting a few incidental references scattered here and there, no systematic quantitative relation between the details of the spectrometer and the resulting curvature of the spectral lines seems to have been found out. In view of the extensive use of rocksalt prisms and linear thermopiles for the examination of the infra-red region, such an investigation is well worth an attempt.

Fig. 1.



In what follows it is assumed that the curvature of the spectral lines arises from the obliquity of the incident rays to the principal plane of the prism, and that the several optical parts are "corrected." The accompanying diagram (fig. 1) represents a prism with its edge  $AA'$  lying wholly in, and the principal plane perpendicular to, the plane of the paper. Let  $PO_1$  be a ray not in the principal plane and  $\theta$  the angle of incidence with the normal  $N_1O_1N_1'$ . The path of the ray  $O_1O_2$  within the prism makes an angle  $\theta'$  with the normal such that  $\sin \theta = \mu \sin \theta'$ . If  $\psi', \psi$  are angles of incidence

\* Communicated by the Authors.

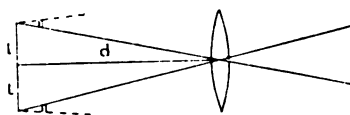
and emergence at the second surface  $\sin \psi = \mu \sin \psi'$ . Since the edge  $AA'$  lies in both the refracting surfaces and the normals  $N_1N_1'$  and  $N_2N_2'$  are perpendicular to the edge, it follows (see Herman's 'Geometric Optics,' xxviii. p. 28) that the incident ray and the emergent ray are equally inclined to the edge. If the rays  $PO_1$ ,  $O_1O_2$ , and  $O_2Q$  are projected on a great circle lying in the principal plane with reference to the edge of the prism as the pole, it is found that the actual deviation  $\delta$  is related to the deviation  $\delta'$  in the projected path by the equation :

$$\sin \frac{\delta}{2} = \sin \beta \cdot \sin \frac{\delta'}{2},$$

where  $\beta$  is the inclination of the ray to the edge of the prism.

Obviously, therefore,  $\delta'$  is always greater than  $\delta$  except when  $\beta = \frac{\pi}{2}$  when, however, the ray lies wholly in the principal plane and the two are equal. In the case of a prism placed in the minimum deviation, radiations from the centre of the slit lie, no doubt, in the principal plane, and

Fig. 2.



those from the extremities do not. If  $2l$  is the length of the slit and  $d$  the distance of the collimating lens from the slit, the maximum possible divergence of the extreme ray is  $\sin^{-1} \frac{l}{(d^2 + l^2)^{\frac{1}{2}}}$ , and therefore  $\sin \beta$  under these conditions is  $\frac{d}{(d^2 + l^2)^{\frac{1}{2}}}$ .

To take the following particular examples :—

(1) In the case of a spectrometer supplied by Adam Hilger & Co., length of the slit  $2l = 1.00$  cm. and  $d = 30$  cm. about ; for a  $60^\circ$  angle prism of crown glass and for mean D line ( $5893 \times 10^{-8}$  cm.)

$$\delta' - \delta = 0^\circ 1' 9'' \cdot 81,$$

and in consequence the resulting curvature of the D line is 0 0006785.

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(2) With the same instrument, but with a  $60^\circ$  angle prism of flint glass and for mean D line

$$\delta' - \delta = 0^\circ 1' 30'' \cdot 23,$$

and the resulting curvature of the D line is **0.0008724**.

(3) In an infra-red spectrometer  $2l = 2$  cm. and  $d$  the distance of the slit from the mirror is about 40 cm.; for a  $60^\circ$  angle prism of rocksalt and for the infra-red region  $1420 \times 10^{-6}$  cm.,  $\mu = 1.5213$

$$\delta' - \delta = 0^\circ 4' 0'' \cdot 13,$$

and the resulting curvature is **0.001163**.

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LXXXVII. *The Striated Discharge in Mercury Vapour.* By  
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#### INTRODUCTION.

**D**URING the past half century a large amount of work has been done on the problem of electrical discharges in rarefied gases. The various parts of the discharge have been studied independently, the Crookes dark space probably receiving most attention, since in this region of the discharge occurs the very interesting phenomenon of the high cathode fall of potential. Much less attention has been given to the negative glow, Faraday dark space, and positive column, which are the subject of this investigation.

Guided by certain theoretical considerations of space-charge and mobility, the experimental results to be described have led to a theory of the mechanism of current flow in the negative glow and Faraday dark space and an explanation of striations in the positive column, which seem satisfactorily to explain the essential features of the discharge.

In order to avoid confusion and unnecessary repetition, the following symbols will be used throughout the following discussion:—

$\mu_+$  and  $\mu_-$  are mobilities of positive ions and electrons respectively;  $M$  and  $m$  are the masses of positive ion and electron;  $V$  is the average velocity of the electrons,  $U_t$  is the terminal velocity of the positive ions, and  $\Omega$  is the velocity of thermal agitation of the atoms, all three being expressed

\* Communicated by Prof. K. T. Compton.

in equivalent volts;  $l$  and  $L$  are the mean free paths of the electrons and the positive ions respectively;  $E$  is the electric intensity;  $c$  and  $C$  are the square root mean square velocities of the electrons and positive ions respectively.

Compton\* gives, as the expression for the mobility of electrons,

$$\mu_- = 0.815 \frac{el}{mc} \dots \dots \dots (1)$$

On the same assumptions, the mobility of the positive ions is found to be

$$\mu_+ = 1.15 \frac{el}{MC}, \dots \dots \dots (2)$$

the difference in numerical factor in the two expressions being due to the fact that the masses of the positive ion and the atom are equal.

On the assumption of elastic collisions between the electrons and the gas molecules, Compton also finds that the terminal energy which an electron will attain, under the influence of an electric field, in the gas, is given by

$$eV_t = \frac{1}{2}e \left[ \Omega + \sqrt{\Omega^2 + \frac{E^2 l^2 M}{1.134m}} \right] \dots \dots \dots (3)$$

On the assumption that the collisions between the positive ions and the gas molecules are as if between elastic spheres and that the law of conservation of momentum holds for the collisions, it is found that, on the average, the positive ion will lose half of its energy on collision if the molecules are considered to be at rest compared with the positive ions. If, however, as is actually more nearly the case, the ions are moving with a velocity  $U$  and the molecules with a velocity  $\Omega$ , the average fraction of energy lost by a positive ion at a collision is given by

$$f = \frac{1}{2} \left( 1 - \frac{\Omega}{U} \right).$$

From this the terminal energy of the positive ions is found to be

$$eU_t = \frac{1}{2}e \left[ \Omega + \sqrt{\Omega^2 + 4.611E^2} \right] \dots \dots \dots (4)$$

by the same reasoning as that by which Compton has obtained the terminal energy of the electrons.

From these equations it is possible by very simple processes to obtain any of the quantities that may be referred to in the course of the present work.

\* Compton, Phys. Rev. xxii. p. 334 (1923).

## THEORY OF THE POSITIVE COLUMN.

Sir J. J. Thomson\* has recently developed the mathematical theory of the striated positive column of the gaseous discharge. According to his theory, the condition for the occurrence of the striations in the positive column of the discharge is that the current density must be lower than a certain critical value which is determined by the rate of recombination of the electrons with positive ions, as well as other quantities which, so far as the author is aware, have not been determined. Consequently, to make further progress in the theory of the striated positive column it is necessary to approach the problem from a different angle.

In experiments on discharges in the so-called "noble gases," it has been found that a striated positive column cannot be obtained if the gas is carefully purified. The author has found the same to be true for mercury vapour, which is to be expected, since it is also a monatomic gas and would therefore be expected to be governed by the same laws. This criterion probably cannot be extended generally to include the multiatomic gases, although the author understands that work done under the supervision of Sir J. J. Thomson in the Cavendish Laboratory points to the conclusion that it is also true for nitrogen. In some of the earliest experiments on gaseous discharges, it was found that mixtures of gases produced the most beautifully striated positive columns†. Thus, in view of the fact that no striations occur in pure monatomic gases, it is natural to conclude that the striations are the direct result of the presence of impurities in the discharge.

In order to account for the striations in the positive column, it is necessary to find conditions which favour ionization at definite regions in the discharge. A shortening of the life of an excited atom will lead directly to this result. In the uniform positive column, atoms exist in every state of excitation, so electrons of almost any speed may produce partial or complete ionization. If, now, the life of an excited atom is diminished by the presence of impurities, it will have to receive the two amounts of energy, necessary to produce ionization, in rapid succession, assuming cumulative ionization. If this is to occur at any point in the positive column, the number of electrons available to supply the energy must be very large; consequently, in order to obtain a uniform positive column with impurities present, the current density

\* Thomson, *Phil. Mag.* xlii. p. 986 (1921).

† J. J. Thomson, 'Conduction of Electricity in Gases.'

in the discharge would have to be large. If, however, the positions of ionization were so localized that a large proportion of the electrons had sufficient energy to produce ionization, considered as a cumulative effect, the probability of ionization would be greatly increased, and the discharge could be maintained at smaller current densities. On making an inelastic collision, the mobility of the electrons is increased, and, as a result, they are drawn at high velocity towards the anode, leaving a positive space-charge where the inelastic collision occurred. A corresponding negative space-charge must exist at some other place, and this will be on either side of the region of ionization. Few of the positive ions travel far before recombination; so, to the cathode side of a region of ionization, a negative space-charge should be found, as there are fewer positive ions to neutralize the space-charge of electrons from the cathode or preceding striation. The resulting distribution of electric intensity tends to continue the ionization in the regions where it started. Thus we have a state which favours localization of ionization and resultant recombination and radiation; in other words, a striated positive column.

The consequences of such a theory of the striations would include several points, which may be checked experimentally:—

1. A higher concentration of excited atoms should exist in the striations than in the space between them. By experiments on the absorption of spectral lines, it should be possible to determine the relative concentrations of excited atoms in different parts of the discharge. This work has been carried out by Compton, Turner, and McCurdy, and the results have been in accord with the theory. An account of this work will appear later.

2. If striations are due to an effect of impurities, these must be of such nature that the energy of an excited atom may be sufficient to transform them into some state of excitation. Franck\* has found that excited mercury atoms will dissociate molecular hydrogen; thus, if hydrogen is used to produce striations in mercury vapour, there should be a greater concentration of atomic hydrogen in the striations than in the regions between them. Any gas which has no critical potential below the lowest radiating potential of mercury should have no effect on the discharge in mercury vapour. Both of these points have been checked experimentally by Compton, Turner, and McCurdy. The presence of atomic hydrogen was detected by the reduction of oxides

\* Franck, *Zeit. f. Phys.* xi. p. 761 (1922).

of metals and the occurrence of the mercury hydride bandspectra.

3. If the above theory is true, the potential difference between successive striations must be sufficient to give the electrons enough energy to produce ionization on travelling from one striation to the next. It was found that, in the case of hydrogen\*, the potential difference between striations was somewhat greater than the ionization potential. Duffendack† found that, in hydrogen, an arc could not be maintained below the ionizing potential; thus cumulative ionization cannot occur in hydrogen. In order to ionize, the electrons must have fallen through a potential equal to the ionizing potential. Also, as collisions of electrons in hydrogen may not be perfectly elastic, the potential difference between striations may be greater than the ionizing potential. For mercury‡ it has been found that the potential difference is about 5 volts. In this case, however, it was assumed that only excitation and not ionization occurred, the current being carried altogether by electrons emitted by the cathode. In the mercury discharge, however, when the current density is large, the density of excited atoms should be sufficient to make cumulative ionization possible. This would make a potential difference between striations of a little over 5 volts sufficient to produce the necessary ionization.

4. The next consequence of this theory is that the concentration of electrons and positive ions should be a maximum near the cathode side of a striation. The current density is the same at all points in the discharge. Thus the concentration of electrons, assuming that they carry practically all the current, should be inversely proportional to the velocity of drift, therefore directly proportional to the velocity of agitation. Also, the concentration of positive ions should be a maximum near the point where they are produced, since they disappear through recombination.

5. The last point to be considered is the distribution of velocities of the electrons. If ionization occurs in the striation, an excess of slow electrons should be found towards the anode side of the striation and in the space between striations. The closest approach to a Maxwellian distribution of velocities should occur just outside the cathode side of the striations, for there the time since the last inelastic collision is a maximum.

\* McCurdy, *Phil. Mag.* xvi. p. 531 (1923).

† Duffendack, *Phys. Rev.* xx. (6) p. 665.

‡ Grotian, *Zeit. f. Phys.* v. p. 148 (1921).

## THEORY OF FARADAY DARK SPACE AND NEGATIVE GLOW.

E. Brose\* has pointed out that the distinction between the negative glow and Crookes dark space is more apparent than real. He shows that the spectral lines occurring in the negative glow extend out into the Crookes dark space, though with diminishing intensity. The same condition holds for the negative glow and the Faraday dark space. Consequently any theory applying to the negative glow should apply equally well to the Faraday dark space.

In the treatment of the positive column, it has been assumed that the current is due to the motion of electrons under the influence of the electric field. This cannot be true in the case of the negative glow and Faraday dark space, for, under such conditions, there would be no logical reason for the marked difference in the appearance of the two regions. Furthermore, a consideration of the efficiency of ionization shows that the number of positive ions produced by the electrons which have fallen through the cathode drop is too large to be received by the cathode without producing impossibly large currents or a space-charge too large to conform to Poisson's equation. The same conclusion may be drawn from the absence of a strong negative space-charge in this region. Very few positive ions would, under normal conditions, penetrate any great distance into the Faraday dark space from the positive column before being lost by recombination, as is proved by the uniformity of the positive column. Therefore, unless positive ions move from the negative glow towards the anode, there should be a negative space-charge in the Faraday dark space which increases from the positive column towards the cathode. This is not found to be the case.

The only alternative that can be postulated is that the current is carried by the diffusion towards the anode of the electrons and positive ions produced in large numbers in the negative glow. This alone cannot fully account for the conditions found in these regions, since the much more rapid diffusion of electrons would still cause a negative space-charge in the Faraday dark space. Therefore there must be an electric field tending to retard the flow of electrons and to accelerate that of the positive ions. A rough calculation of the field necessary to produce the observed results has been carried out; and although by no means rigorous, it shows that a very small field is sufficient to account for the observed

\* Brose, *Ann. d. Phys.* lviii. p. 731 (1919).

conditions. This field would be automatically set up and adjusted by the mobilities and rates of diffusion.

The net current must be an electron current from the negative glow to the positive column, so, to get an estimate of the field which may exist, let us assume that the resultant current is the difference between an electron diffusion current in the positive direction and an electron conduction current in the negative direction. This will give an upper limit to the field which can exist and still allow the observed current to flow.

$$i = D_e \frac{dN}{dx} - \mu_- N e E,$$

where  $i$  represents the current density,  $D$  the coefficient of diffusion and  $N$  the electron density.

Since

$$D = \frac{kT}{e} \mu = \frac{2}{3} V \mu, \quad i = \mu e \left( \frac{2}{3} V \frac{dN}{dx} - EN \right).$$

This must be positive; and also  $\frac{dN}{dx}$  is found experimentally to be of the same order of magnitude as  $N$ . Therefore  $E$  must be less than  $\frac{2}{3} V$ . This is of the order of 1 volt, so the electric field must be less than 1 volt per centimetre. It is quite possible that small gradients of this order might not be detected, since in measurements it is difficult to obtain very constant conditions.

Thus, to support the diffusion hypothesis, one should find a strong concentration of electrons and positive ions in the negative glow and Faraday dark space, and a strong concentration gradient diminishing towards the positive column, and, possibly, a negative potential gradient at the anode side of the negative glow.

The following work was carried out in an attempt to confirm the theories just advanced concerning both positive column and Faraday dark space. Mercury vapour was used, as the simplest possible conditions should exist with a monatomic gas. Also more critical data are known for mercury than for most of the other gases.

#### METHOD.

Several methods have been employed in the study of the discharge, the three most important of these being:—

1. The study of potential distribution by means of the deflexion of a beam of cathode rays developed by Aston\*.

\* Aston, Proc. Roy. Soc. A, lxxxiv. p. 526 (1911).

This method, however, is limited in application, since it can be used only at low pressures.

2. The Stark effect produced on lines of the spectrum emitted by atoms in an electric field\*. This method is limited in application to the case of strong fields, since the effect is very small.

3. The use of an exploring electrode introduced into the path of the discharge, and a measurement of the potential which it acquires†. Objections have been raised against this method on the grounds that it may not take up the potential of the gas surrounding it, due to the inequalities of velocities of electrons and positive ions and also to non-uniform density of ions of the two signs.

The method selected for the following work is a modification of the one last named. It was first suggested by Langmuir‡, and applied to the study of the uniform positive column of the mercury-vapour discharge.

If a wire is introduced into the path of a discharge and maintained at a potential negative to that of the surrounding gas, positive ions are accelerated towards it and electrons are repelled. The result is that the wire is surrounded by a positive space-charge sheath. The outside of this sheath is at the potential of the surrounding space, and the inside at that of the wire. The positive ion current to the wire is limited by space-charge, and may to a first approximation be considered as a space-charge current between concentric cylinders. As the potential of the wire is raised, electrons reach the wire against the field until, finally, enough electrons get in to just neutralize the positive ion current, but not enough to neutralize the positive space-charge around the wire, so the positive ion current is still limited by space-charge. This gives the apparent potential of the space as determined by the old exploring electrode and electrometer method, but actually the wire is still negative with respect to the gas. As the potential of the wire is still further raised, the electron current to it increases. This current should be expressible as a function of the potential difference between the outside and inside of the space-charge sheath by the following equation, if there is a Maxwellian distribution of velocities of the electrons:

$$I = N_0 e \sqrt{\frac{eV}{3\pi m}} e^{-\frac{3(V_0 - V)}{2V}} \dots \dots (5)$$

\* E. Brose, *loc. cit.*

† Thomson, *Cond. in Gases*, p. 530.

‡ Langmuir, *Journal of Franklin Inst.* Dec. 1923; (*Gen. Elec. Rev.* xxvi, p. 731 (1923)).



Therefore  $\log I$  as a function of  $V_0 - V$  should be a straight line, where  $I$  is the current density to the wire, and  $V_0$  and  $V$  the potentials of the space and wire respectively.

When the wire is at the potential of the space, the law regulating the current to it changes. Above this no positive ions can reach the wire, so now the wire will be surrounded by a negative space-charge sheath. The thickness of this sheath will change more rapidly in the case of the electrons than for the positive ions, and as a result no simple relation can be expected to exist between the current and the applied potential. However, since a change in condition occurs as the potential of the space is passed, a "break" is found in the  $\log I$ -voltage curve. The position of this "break" locates the true potential of the gas.

From these  $I$ - $V$  curves (of the exploring electrode) it is possible to obtain some very interesting data.

*Average Energy of Electrons.*—Assuming a Maxwellian distribution of velocities of the electrons, it is readily seen from equation (5) that the average energy of the electrons may be determined directly from the current-voltage curves. Transforming the equation by taking the logarithms of both sides,

$$\log I = \log N_0 e \sqrt{\frac{eV}{3\pi m}} - \frac{3}{2} \frac{V_0 - V}{\bar{V}} \quad (6)$$

Thus the slope of the curve  $\log I$  as a function of  $V$  is connected with the average velocity in volts by the relation

$$\bar{V} = \frac{3}{2 \tan \theta} \quad (7)$$

If the distribution is not according to Maxwell's law, the only method of determination of the average energy is by actual integration of the current curves. This process was carried out in a few cases.

*Concentration of Electrons.*—Although not in all cases is the distribution of speeds according to Maxwell's distribution law, still it is possible to obtain at least an approximate value for the electron concentration. From equation (5) it is observed that when  $V_0 - V = 0$  the electron concentration as a function of the current is given by

$$N_0 = \frac{I}{e} \sqrt{\frac{3\pi m}{eV}} \quad (8)$$

This serves as a ready means of obtaining the electron concentration, since all the quantities are either known or can be obtained from the curves.

*Concentration of Positive Ions.*—The determination of the positive ions is not so direct and simple as for electrons. More approximations have to be made in the calculation, and consequently the results cannot be expected to be quite so satisfactory. An approximate calculation may be carried out as follows :—

Assuming that the positive ion current to the wire at a known negative potential  $V$  with respect to the surrounding space is a positive ion space-charge current between coaxial cylinders, Langmuir's\* space-charge equation

$$C = \frac{2\sqrt{2}}{9} \sqrt{\frac{e}{M}} \frac{V^{3/2}}{(-r\beta^2)}, \quad \dots \quad (9)$$

where  $C$  is the current per unit length of the wire and  $r$  is its radius, may be used. From this it is possible to calculate the value of the quantity  $(-\beta^2)$ , and thus the radius of the outside surface of the space-charge sheath can be determined from the tables given by Langmuir. Thus, if a Maxwellian distribution is assumed, as has been done for electrons, it is possible to calculate the positive ion concentration directly. It is that concentration such that all positive ions striking the outer layer of the sheath contribute to the observed positive ion current. The equation involved is the same as that used for electrons with proper substitutions for the values of  $M$  and  $U$ . The method used for the determination of the energy of the positive ions is by calculation, using equation (4) for the terminal energy.

*Correction to be applied to the potential determinations by the electrometer method.*—This is found directly by taking the difference between the voltage of the point where zero current arrives at the wire and that where the "break" in the current-voltage curve occurs.

#### APPARATUS.

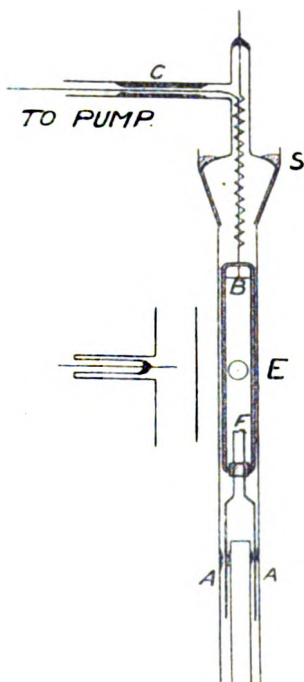
A diagram of the apparatus used in this work is given in fig. 1. The main tube, of 1.5 inch diameter, was enclosed in an electric furnace which extended about twelve inches below the level of the mercury in the two small tubes marked **A** on the diagram. These tubes dipped into mercury wells so adjusted as to bring the level of the mercury almost to the base of the discharge-tube. The mercury in these served as a source of vapour for the discharge, and also as a

\* Langmuir, Phys. Rev. xxii. p. 347 (1923).

means of connecting the filament F which served as cathode for the discharge. The object of using the hot cathode was to obtain currents of considerable magnitude without the use of very high potentials.

The filament F and anode B were fixed in a light glass frame which was movable inside the discharge-tube and so arranged that the length of the discharge could be easily adjusted by altering the position of the anode in the frame.

Fig. 1.



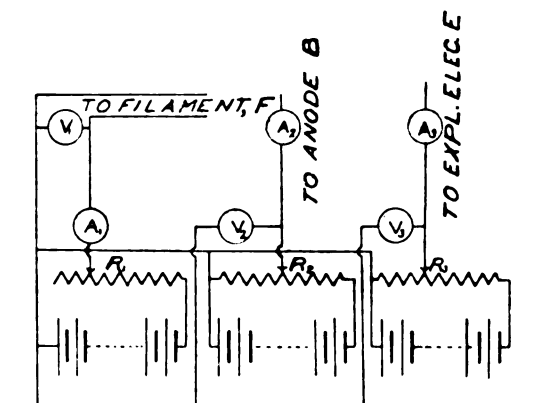
The anode was an iron disk, electrically connected through the spiral shown at the top of the tube, and the position of the frame was adjusted by means of the fine wire communicating through the capillary tube C with a winch not shown on the diagram. The capillary was inserted to allow as nearly constant pressure conditions in the discharge-tube as possible.

The exploring electrode was a piece of 4 mil tungsten wire,

and was covered with glass to within a few millimetres of the end and placed as near as possible to the centre of the discharge-tube.

The electrical connexions are shown in fig. 2. The resistance  $R_2$  served as a potentiometer to vary the potential of the exploring electrode. The current to the electrode was measured on the microammeter  $A_3$  and its potential by the voltmeter  $V_3$ .

Fig. 2.



Readings of the current to the electrode were made at intervals of 0.5 volt from about 1 volt below the point where the current changed sign to several volts above. The results were plotted on semi-log. paper to make the calculations involved easier.

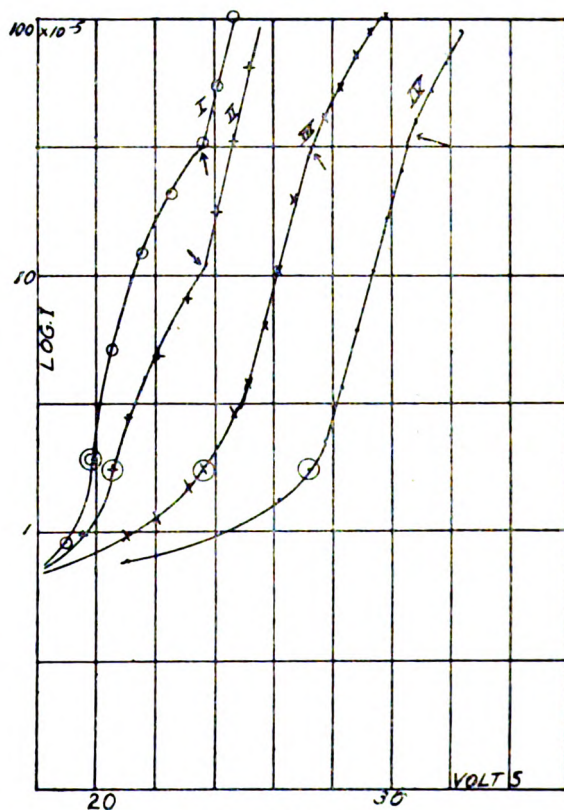
In plotting, only the electron current was wanted; therefore the positive ion current at a definite voltage below that of the space was added to the negative current as indicated by the ammeter, for this was considered to give the electron current near enough to the true value to satisfy other conditions of the work. Care was taken, however, to measure the positive ion current at a voltage sufficiently below that of the space to insure that no appreciable number of electrons reached the wire.

### RESULTS.

A set of four typical curves representing the current-voltage relation found in the various parts of a striation are shown in fig. 3.

The values of the potential distribution in a striation cannot be taken from fig. 3. It was necessary to so arrange the curves as to make them as distinct as possible rather than to give the distribution of potential over a striation.

Fig. 3.



Curve No. I. was taken with the exploring electrode between two striations;

Curve No. II. at the anode side of a striation;

Curve No. III. in the middle of a striation; and

Curve No. IV. at the cathode side of the striation.

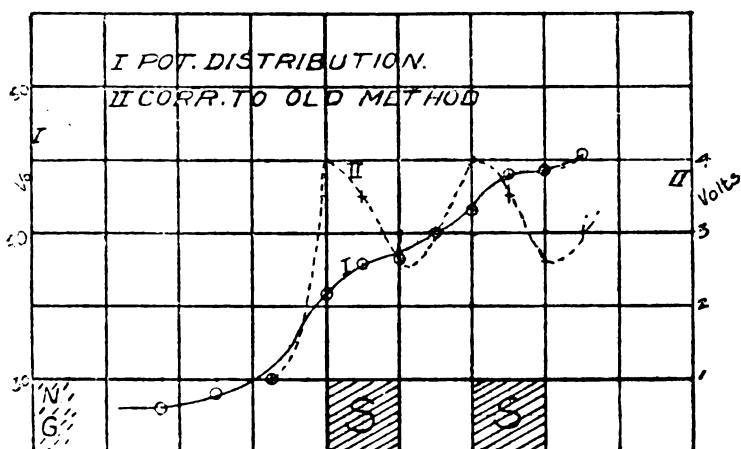
The circles represent the potential of the space as given by the old exploring electrode method. The arrows represent the true potential of the space.

It will be observed from the figure that the discontinuity giving the true potential of the space, indicated by the arrow, does not occur in the same direction in all cases.

The reason for this is not very clear. In order to determine whether or not the correct point was chosen, the potential of the space was determined also by means of a hot-filament exploring electrode, the true potential of the space being given by the highest potential which can be applied to the hot filament without stopping its thermionic emission. This method has been shown to give correct values, even in the electric field with no discharge flowing. The two methods checked within the experimental accuracy of the work.

Fig. 4 gives the general character of the distribution of potential in the discharge, and the broken curve gives the

Fig. 4.



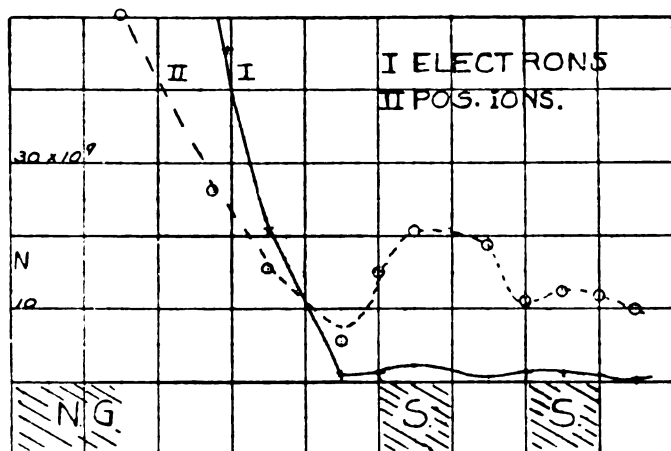
difference between the results of the current method and the usual, but less accurate, electrometer method of measuring potentials.

It will be observed that the potential distribution curves show the general characteristics of the distribution curves found in any work on gaseous conduction. They indicate a positive space-charge near the cathode face of the striations, and a negative space-charge between the striations. It will further be observed that the correction that must be applied to the electrometer determination of potential changes from place to place in the striations. It is a maximum near the cathode side of the striation and a minimum in the space between the striations. This is what would be expected

on the theory advanced to explain the striations and the processes occurring in the discharge.

Fig. 5 shows the variation in the concentration of the electrons and the positive ions at various points in the striations. In agreement with the theory, it is found that the concentration of both positive ions and electrons is a maximum near the cathode side of the striation and a minimum in the space between them. No claim to great accuracy is made regarding the numerical values of these concentrations, since too many approximations are necessary in the determinations. Still, as the conditions are comparatively constant,

Fig. 5.



the relative values shown should be comparable and the order of magnitude of the results should be reliable. The positive ion concentration is in all cases too large, and some of the sources of error will be discussed later.

Table I. shows the numerical results of a typical run, and the energies of the electrons as calculated from the curves.

#### DISCUSSION OF RESULTS.

As has been already pointed out, very small accuracy can be claimed for work of this nature. The discharge itself is too sensitive to small changes of conditions of the tube; also the assumptions which underlie the calculations of the quantities given cannot be accurately fulfilled. However, as an approximation to the true values, the results may be considered to be of some importance. The more important sources of error will be taken up separately.

TABLE I.

V.	$V_0$	$V_0 - V.$	$i+$ , $\times 10^{-6}$	$i-$ , $\times 10^{-5}$	$\bar{V}$ .	$N-$ , $\times 10^3$	$r_+$ , $\times 10^{-2}$	$N+$ , $\times 10^3$	Position.
54.5	57.4	2.9	4.9	1.5	1.2	.38	8.0	10.0	Between striations.
53.6	57.3	3.7	5.0	3.5	1.5	.75	7.4	11.8	Anode side of striation.
51.9	56.6	4.7	5.7	6.0	1.4	1.30	7.5	12.4	Middle of striation.
50.2	54.2	4.0	5.2	7.6	1.7	1.55	7.2	11.0	Cathode side of striation.
48.3	51.7	3.4	2.9	3.0	1.5	.65	8.5	5.6	1.3 mm. into F.D.S.
48.1	49.2	1.1	5.0	5.0	.40	21.0	5.4	15.5	1.3 mm. into F.D.S.
48.7	49.6	.9	7.2	100	.24	53.5	4.6	26.2	20 mm. into F.D.S.
48.9	50.0	1.1	5.5	25.0	.40	101.0	1.8	51.5	Anode side of negative glow.
48.8	50.1	1.3	4.75	47.0	.91	130.0	.9	900.0	Middle of negative glow.

Discharge at temperature 85°, mercury-vapour pressure = 0.12 mm.

Current in discharge was 12.5 mill amperes; potential across tube 86 volts.

V is potential of space by old method;  $V_0$  the true potential of space;  $i+$ , the positive ion current to the wire at a known voltage below  $V_0$ ;  $i-$ , the electron-current to the electrode at  $V_0$ ;  $N-$ , the electron concentration;  $r_+$ , the radius of the sheath; and  $N+$ , the positive ion concentration.



*Initial Velocities of the Positive Ions.*—The positive ions on passing into the region of the space-charge sheath from the surrounding gas will have an initial velocity. The effect of this will be two-fold: (1) the positive ion current will somewhat exceed the value limited by Langmuir's original space-charge equation, which assumed zero initial velocity; and (2) all the ions that pass into the sheath may not reach the wire. In the determination of the positive ion density it was assumed that all ions reached the wire. An approximate calculation of the number of ions which fail to reach the electrode has been carried out based on the assumption that no collisions of the ions with gas molecules occur, which is the most unfavourable condition. If an ion passes into the positive ion sheath with a velocity  $U$  in a direction making an angle  $\phi$  with the radius of the cylinder to the point, and the laws of (1) conservation of energy, (2) conservation of angular momentum are applied, it is found that the condition for the ion to reach the wire is given by the relation

$$\sin \phi < \frac{b}{a} \sqrt{1 - \frac{V}{U}},$$

where  $V$  is the potential difference between the wire and the outside of the sheath,  $a$  and  $b$  the radii of the outside of the sheath and the wire respectively. From this it is seen at once that if  $V$  is of the order of 20 volts, and since  $U$  is of the order of 0.05 volt as calculated from the terminal velocity of the positive ions, all the ions will reach the wire provided that the ratio of the radii of the wire to the outside of the sheath is 1:20. If the sheath becomes larger than this, some of the ions which pass inside it will not reach the wire owing to their angular momentum. Care was taken in the calculations to see that this condition was satisfied.

*The effect of the ends of the wire on the calculation of concentration.*—If the radius of the sheath becomes large, the area of the two hemispherical ends which close the assumed cylindrical volume may become important. This factor was taken into consideration by assuming that the current density across the boundary of the sheath was the current to the wire divided by the total area of the sheath. This factor would also affect the calculation of the thickness of the sheath from the space-charge current equation. However, as the area of the ends was only about 20 per cent. of the area of the sides, this should not be an important source of error.

*Velocity of Drift of the Positive Ions.*—From the expressions

for the mobility and the terminal velocity of the positive ions it is found that, under the conditions applying to the discharge, the velocity of drift of the positive ions is comparable with that of thermal agitation. The above equations were based on the assumption of no velocity of drift. In order to arrive at an estimate of the error introduced by this, we may consider that the ions are made up of two groups:—

- (1) Those which have a velocity of thermal agitation only, and
- (2) Those which have a velocity of drift.

The relative numbers of ions in the two groups will be in the ratio of the velocities; the effective collecting areas of the two will be in the ratio of the area of the outside of the sheath to the area of the section of the sheath by a plane along the axis of the wire and at right angles to the axis of the tube—*i.e.*, in the ratio of  $2\pi rL : 2rL$ . This fact has been taken into account in the calculations of the concentrations given.

This, of course, cannot be considered to represent the actual facts of the case, for what really occurs is that the ions must be considered to have a Maxwellian distribution of velocities about a velocity of drift. However, statistically the two conditions would produce about the same results.

*The effect of drawing the Positive Ions out of the Discharge.*—The calculated value of the positive ion concentration is found still to be larger than that of the electrons after the above corrections have been made. A possible explanation of this may be found in the fact that all the positive ions which pass into the sheath are lost to the gas. Thus a negative space-charge should build up around the sheath, since electrons are reflected from the space by the electric field. This condition complicates the problem by the addition of an extra space-charge sheath between the wire and the undisturbed gas, and thus the positive ions which reach the wire do not arrive there simply by thermal motion, but are also drawn in by the electric field due to the negative space-charge. A mathematical treatment of this appears to involve so many unknown quantities that it is hopeless to attempt to obtain a satisfactory solution of the problem. However, it can readily be seen that the result will be a reduction in the positive ion concentration, though the amount of this reduction cannot readily be estimated.

*Concentration of the Electrons.*—The most obvious source of error in the determination of the concentration of the

electrons is the absence of an exact Maxwellian distribution of velocities. There seems to be no simple way of correcting for this factor, though it is probably not very important for small departures. Another source of difficulty is the fact that the glass covering of the exploring electrode becomes coated with a semi-conducting film after it has been in the discharge for some time. Successive runs under as nearly similar conditions as possible show that this error is not very serious.

A check on the electron concentration is possible on the assumption that the current in the positive column is totally one of conduction and carried entirely by the electrons. Making use of the mobility of the electrons as given above and the electric intensity as measured, it is possible to calculate the electron concentration necessary to account for the current. By carrying out a determination of this sort, it has been found that the result gives an electron concentration about three times that calculated from the other method. This agreement is probably as good as can be expected from work of this sort.

#### SUMMARY.

The theory is advanced that the striations which occur in the positive column of the discharge in a monatomic gas under low pressure are due to the presence of impurities; and also that the current in the positive column of the discharge is due to the motion of electrons under the influence of the electric field, while that in the Faraday dark space and the negative glow is due to diffusion of electrons and positive ions produced in the negative glow by the fast electrons from the Crookes dark space.

The experimental results confirm the theories advanced in the following important respects:—

(1) The potential distribution in the discharge satisfies the theory as regards the distribution of space-charge.

(2) The concentration of the electrons is found to be a maximum near the cathode side of the striations. Also that of the positive ions, but the variation in the case is not so marked.

Further, it is found that the corrections that must be applied to the determination of potential in the discharge by the old exploding electrode method vary from point to point in the striations and are a maximum near the cathode side of the striation.

(3) A reverse field may exist in part of the negative glow,

but the concentration gradient of the electrons in the negative glow and Faraday dark space is found to be amply sufficient to account, by diffusion, for the currents observed in the discharge.

In conclusion, I wish to express my sincere thanks to Professor K. T. Compton, under whose supervision this work was carried out, for the interest he has taken and the assistance rendered throughout the course of the work; also to Dr. Irving Langmuir, who suggested the method for using the exploring electrode in advance of his publication, and who gave other valuable suggestions.

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LXXXVIII. *The Relations between Antisymmetric Tensors and Tensor-Densities.* By P. DU VAL \*.

THE object of this paper is to point out certain relations, not apparent in the usual treatment of the subject, between antisymmetric tensors and tensor-densities of various ranks. The four-dimensional case only will be discussed, though similar considerations apply to the tensor analysis in any number of dimensions.

§ 1. *Change of Coordinates.*

In the four-dimensional world let the coordinates, in two different systems, of the field-point be  $x_\mu$  and  $x'_\mu$ ; let  $\cdot A^\mu$ ,  $\cdot A'^\mu$  be the components, in the same two systems, of a contravariant vector; then the law of transformation of vector-components with change of coordinates is

$$\cdot A'^\mu = \frac{\partial x'_\mu}{\partial x_\alpha} \cdot A^\alpha, \quad . . . . . \quad (i.)$$

where the summation convention gives one term on the right for each suffix  $\alpha$ .

Similarly, if  $\cdot A^{\mu\nu}$  be an antisymmetric contravariant tensor of the second rank,

$$\cdot A'^{\mu\nu} = \frac{\partial x'_\mu}{\partial x_\alpha} \frac{\partial x'_\nu}{\partial x_\beta} \cdot A^{\alpha\beta},$$

\* Communicated by the Author.

where the summation on the right is with respect to  $\alpha$  and  $\beta$  independently—i. e., there is one term for each of the sixteen permutations  $\alpha\beta$ . Four of these terms vanish, however, and since  $\cdot A^{\alpha\beta} + \cdot A^{\beta\alpha} = 0$ , the equation becomes

$$\cdot A'^{(\mu\nu)} = \frac{\partial(x'_{\mu}, x'_{\nu})}{\partial(x_{\alpha}, x_{\beta})} \cdot A^{(\alpha\beta)}, \quad . \quad . \quad . \quad . \quad (ii.)$$

where the enclosure of  $(\alpha\beta)$  in brackets indicates that the summation is to give one term for each of the six such combinations. Only antisymmetric groups of suffixes will be enclosed in this way.

In the same way, if  $\cdot A^{\mu\nu\rho}$  be an antisymmetric contra-variant tensor of the third rank,

$$\cdot A'^{(\mu\nu\rho)} = \frac{\partial(x'_{\mu}, x'_{\nu}, x'_{\rho})}{\partial(x_{\alpha}, x_{\beta}, x_{\gamma})} \cdot A^{(\alpha\beta\gamma)}, \quad . \quad . \quad . \quad (iii.)$$

and if  $\cdot V^{\mu\nu\rho\sigma}$  be one of the fourth rank,

$$\cdot V'^{(\mu\nu\rho\sigma)} = \frac{\partial(x'_{\mu}, x'_{\nu}, x'_{\rho}, x'_{\sigma})}{\partial(x_{\alpha}, x_{\beta}, x_{\gamma}, x_{\delta})} \cdot V^{(\alpha\beta\gamma\delta)}.$$

In this case, as there is only one component we may represent its magnitude (for a positive permutation of the suffixes 1 2 3 4) by  $\cdot V$ , finding

$$\begin{aligned} \cdot V' &= \frac{\partial(x'_1, x'_2, x'_3, x'_4)}{\partial(x_1, x_2, x_3, x_4)} \cdot V \\ &= D \cdot V. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iv.) \end{aligned}$$

The corresponding equations for antisymmetric covariant tensors are, of course,

$$\cdot A'_{\mu} = \frac{\partial x_{\mu}}{\partial x'_{\alpha}} \cdot A_{\alpha}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (v.)$$

$$\cdot A'_{(\mu\nu)} = \frac{\partial(x_{\mu}, x_{\nu})}{\partial(x'_{\alpha}, x'_{\beta})} \cdot A_{(\alpha\beta)}, \quad . \quad . \quad . \quad . \quad (vi.)$$

$$\cdot A'_{(\mu\nu\rho)} = \frac{\partial(x_{\mu}, x_{\nu}, x_{\rho})}{\partial(x'_{\alpha}, x'_{\beta}, x'_{\gamma})} \cdot A_{(\alpha\beta\gamma)}, \quad . \quad . \quad . \quad (vii.)$$

$$\cdot V'_{(\mu\nu\rho\sigma)} = \frac{\partial(x_{\mu}, x_{\nu}, x_{\rho}, x_{\sigma})}{\partial(x'_{\alpha}, x'_{\beta}, x'_{\gamma}, x'_{\delta})} \cdot V_{(\alpha\beta\gamma\delta)}.$$

$$\cdot V' = D^{-1} \cdot V. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (viii.)$$

It is clear, moreover, that a tensor density undergoes the same transformations as the corresponding tensor, and is in addition multiplied by  $D^{-1}$ . . . . . (ix.)

§ 2. *General Transformation of Linear Tensors.*

We now make the definition of a linear tensor of type  $r$ : we suppose  $r$  to be expressed in the two forms

$$r \equiv 4m + p \equiv -(4n + q),$$

where  $m$  and  $n$  are integers and  $0 \leq p \leq 4$ ,  $0 \leq q \leq 4$ . This gives that  $p + q = 4$ . If  $p = 1$ ,  $q = 3$ , we call the tensor a displacement-tensor; if  $p = q = 2$ , we call it a surface-tensor; if  $p = 3$ ,  $q = 1$ , a space-tensor; and if  $p = 0$ ,  $q = 4$  or  $p = 4$ ,  $q = 0$ , a scalar.

A linear tensor of the  $r$ th type has  $\frac{4!}{p!q!}$  components, which may be distinguished by antisymmetric combinations either of  $p$  upper suffixes or of the remaining  $q$  lower suffixes. One more than the highest (positive or negative) multiple of 4 which occurs in  $r$  is indicated by the number of (upper or lower) dots which precede the symbol; thus, if  $\mu \dots \rho \dots$  be a positive permutation of 1 2 3 4, with  $p$  suffixes  $\mu \dots$  and  $q$  suffixes  $\rho \dots$ ,

$${}^{m+1}A^{\mu\dots} = {}_{n+1}A_{\rho\dots}$$

is a linear tensor of type  $r$ . [Here  ${}^{m+1}$  and  ${}_{n+1}$  are used to indicate  $m+1$  upper and  $n+1$  lower dots; this will in general be unnecessary, as more than two dots do not ordinarily occur.] In any change of coordinates the corresponding transformation is

$$\left. \begin{aligned} {}^m A'^{\mu\dots} &= D^m \frac{\partial(x'_{\mu}, \dots)}{\partial(x_{\alpha}, \dots)} {}^m A^{\alpha\dots}, \\ {}_n A'_{\rho\dots} &= D^{-n} \frac{\partial(x'_{\rho}, \dots)}{\partial(x'_{\epsilon}, \dots)} {}_n A_{\epsilon\dots} \end{aligned} \right\} \dots \dots (x.)$$

The equivalence of these two equations follows immediately from the identity

$$\frac{\partial(x'_{\rho}, \dots)}{\partial(x'_{\epsilon}, \dots)} = \frac{\partial(x'_{\mu}, \dots)}{\partial(x_{\alpha}, \dots)} / D.$$

It is easily seen that the equations (i.) ... (ix.) are all

cases of (x.), and hence that antisymmetric tensors and tensor densities of all ranks are by definition linear tensors, in accordance with the following table :—

Type.	Antisymmetric Tensors.	Antisymmetric Tensor-Densities.
+4	Contravariant, 4th rank.	
+3	„ 3rd rank.	
+2	„ 2nd rank.	
+1	„ 1st rank.	
0	Invariant.....	Contravariant, 4th rank.
-1	Covariant, 1st rank.....	„ 3rd rank.
-2	„ 2nd rank .....	„ 2nd rank.
-3	„ 3rd rank .....	„ 1st rank.
-4	„ 4th rank .....	Invariant-Density.
-5	.....	Covariant, 1st rank.
-6	.....	„ 2nd rank.
-7	.....	„ 3rd rank.
-8	... ..	„ 4th rank.

### § 3. The Grassmann Product.

Clearly, in multiplying two linear tensors the summation will act differently according as we use upper or lower suffixes. It will thus be convenient to have a notation for products independent of the summation-convention and the position of the suffixes.

In general, we define the Grassmann product of two linear tensors as that obtained by writing the first with  $p_1$  upper suffixes and the second with  $q_2$  lower suffixes, and contracting; if  $p_1 < q_2$ , we make the  $p_1$  upper the same as the first  $p_1$  lower suffixes; if  $p_1 = q_2$ , we make each upper the same as the corresponding lower suffix; if  $p_1 > q_2$ , we make the  $q_2$  lower the same as the last  $q_2$  upper suffixes; both the  $p_1$  and the  $q_2$  suffixes being in brackets, so that the summation is by combinations of suffixes. The three types of products corresponding to  $p_1 < q_2$ ,  $p_1 = q_2$ ,  $p_1 > q_2$  are called progressive, scalar, and regressive respectively.

The Grassmann product is conveniently represented by enclosing the two factors within square brackets, the suffixes being replaced by an upper dot for a displacement tensor, a lower dot for a space tensor, and one in an intermediate position for a surface tensor.

It is easily verified that the Grassmann product is commutative if at least one of the factors is a surface tensor; but if neither is a surface tensor, the product

is anticommutative. Moreover, the product of three or four displacement or space tensors, or of two displacement or space tensors and one surface tensor, is associative.

Expressions for progressive products where both factors are written with upper suffixes, and for regressive where both are written with lower suffixes, are important.

I. Progressive :

$$[A \cdot B]^{(\mu\nu)} = -[B \cdot A]^{(\mu\nu)} = - \begin{vmatrix} A^\mu & A^\nu \\ B^\mu & B^\nu \end{vmatrix}, \quad \dots \quad (\text{xi.})$$

$$[A \cdot B]^{(\mu\nu\rho)} = [B \cdot A]^{(\mu\nu\rho)} = A^\mu B^{\nu\rho} + A^\nu B^{\rho\mu} + A^\rho B^{\mu\nu}, \quad \dots \quad (\text{xii.})$$

$$[A \cdot B \cdot C]^{(\mu\nu\rho)} = - \begin{vmatrix} A^\mu & A^\nu & A^\rho \\ B^\mu & B^\nu & B^\rho \\ C^\mu & C^\nu & C^\rho \end{vmatrix}, \quad \dots \quad (\text{xiii.})$$

$$[A \cdot B \cdot C \cdot D] = \begin{vmatrix} A^1 & A^2 & A^3 & A^4 \\ B^1 & B^2 & B^3 & B^4 \\ C^1 & C^2 & C^3 & C^4 \\ D^1 & D^2 & D^3 & D^4 \end{vmatrix} \dots \quad (\text{xiv.})$$

II. Regressive :

$$[A \cdot B]_{(\mu\nu)} = -[B \cdot A]_{(\mu\nu)} = - \begin{vmatrix} A_\mu & A_\nu \\ B_\mu & B_\nu \end{vmatrix} \dots \quad (\text{xv.})$$

$$[A \cdot B]_{(\mu\nu\rho)} = [B \cdot A]_{(\mu\nu\rho)} = A_\mu B_{\nu\rho} + A_\nu B_{\rho\mu} + A_\rho B_{\mu\nu}, \quad \dots \quad (\text{xvi.})$$

$$[A \cdot B \cdot C]_{(\mu\nu\rho)} = - \begin{vmatrix} A_\mu & A_\nu & A_\rho \\ B_\mu & B_\nu & B_\rho \\ C_\mu & C_\nu & C_\rho \end{vmatrix} \dots \quad (\text{xvii.})$$

$$[A \cdot B \cdot C \cdot D] = \begin{vmatrix} A_1 & A_2 & A_3 & A_4 \\ B_1 & B_2 & B_3 & B_4 \\ C_1 & C_2 & C_3 & C_4 \\ D_1 & D_2 & D_3 & D_4 \end{vmatrix} \dots \quad (\text{xviii.})$$



In these formulæ the preceding dots are omitted, as the expressions are just the same whatever the arrangement of these may be.

#### § 4. Other Tensors.

A tensor of type  $(4m + p_1 + p_2 + \dots - q_1 - q_2 - \dots)$  is one which has components with  $\Sigma(p)$  upper suffixes, of which the first group of  $p_1$ , the next group of  $p_2$ , etc., are each antisymmetric amongst themselves, and  $\Sigma(q)$  lower suffixes, of which the first group of  $q_1$ , the next group of  $q_2$ , etc., are each antisymmetric amongst themselves; *i. e.*, if there are  $p_1$  suffixes  $(\mu\dots)$ ,  $p_2$  suffixes  $(\rho\dots)$ , ...,  $q_1$  suffixes  $(\theta\dots)$ ,  $q_2$  suffixes  $(\sigma\dots)$ , etc., then  $T_{(\theta\dots)(\sigma\dots)}^{(\mu\dots)(\rho\dots)\dots}$ , preceded by dots corresponding to one more than the highest multiple of 4 contained in  $4m + \Sigma(p) - \Sigma(q)$ , is such a tensor. It is transformed according to the law (*cf.* the law (x.)) :

$$T_{(\theta\dots)(\sigma\dots)}^{(\mu\dots)(\rho\dots)\dots} = D^m \frac{\partial(x'_\mu, \dots)}{\partial(x_\alpha, \dots)} \frac{\partial(x'_\rho, \dots)}{\partial(x_\epsilon, \dots)} \dots \\ \frac{\partial(x_\theta, \dots)}{\partial(x'_\zeta, \dots)} \frac{\partial(x_\sigma, \dots)}{\partial(x'_\lambda, \dots)} \dots T_{(\zeta\dots)(\lambda\dots)}^{(\alpha\dots)(\epsilon\dots)\dots} \quad (\text{xix.})$$

We may, of course, replace any group of  $p_r$  upper suffixes by a lower group of the remaining  $4 - p_r$ , and each lower group of  $q_r$  by an upper group of the remaining  $4 - q_r$ , altering  $m$  so as to keep the sum  $4m + \Sigma(p) - \Sigma(q)$  unchanged. In general, also, it will be necessary to distinguish the order of the suffix-groups, upper and lower together; thus  $T_{(\theta\dots)(\sigma\dots)}^{(\mu\dots)(\rho\dots)}$  ... is different from  $T_{(\theta\dots)(\sigma\dots)}^{(\mu\dots)(\rho\dots)}$  ..., or from  $T_{(\theta\dots)}^{(\mu\dots)(\rho\dots)}_{(\sigma\dots)}$  ..., etc.

The  $n$ -ple product of two tensors is formed by taking the last  $n$  suffix-groups of the first, and the first  $n$  groups of the second, each with each, *i. e.* (if there are  $m + n$  groups in the first tensor) the  $(m + 1)$ th of the first with the 1st of the second, the  $(m + 2)$ th of the first with the 2nd of the second, etc., and treating these pairs of groups separately as though to form a Grassmann product.

Thus, to take an instance at random, the double product of  $T_{(\rho\sigma)}^{(\mu\nu)(\alpha\beta\gamma)}$  and  $E_{\eta\lambda\theta\phi}$  is

$$[[T \cdot E]]_{(\rho\sigma\eta)}^{(\mu\nu)(\alpha)} = T_{\rho\sigma}^{(\mu\nu)} E_{\eta(\beta\gamma)}^{(\alpha\beta\gamma)} + T_{\sigma\eta}^{(\mu\nu)} E_{\rho(\beta\gamma)}^{(\alpha\beta\gamma)} \\ + T_{\eta\rho}^{(\mu\nu)} E_{\sigma(\beta\gamma)}^{(\alpha\beta\gamma)},$$

since the Grassmann product of  $T_{(\rho\sigma)}$  and  $E_\eta$  is  $T_{\rho\sigma}E_\eta + T_{\sigma\eta}E_\rho + T_{\eta\rho}E_\sigma$ , and that of  $T^{(\alpha\beta\gamma)}$  and  $E_{(\theta\phi)}$  is  $T^{(\alpha\beta\gamma)}E_{(\beta\gamma)}$ .

A tensor of the second rank, whether contravariant or covariant, gives by repeated double multiplication into itself other tensors; take, for instance, any covariant tensor of the second rank,  $P_{\mu\alpha}$ ; from it we derive :

$$\left. \begin{aligned} P_{(\mu\nu)(\alpha\beta)} &= \frac{1}{2} [[P..P..]]_{\mu\nu(\alpha\beta)} \\ &= \begin{vmatrix} P_{\mu\alpha} & P_{\mu\beta} \\ P_{\nu\alpha} & P_{\nu\beta} \end{vmatrix}, \\ P_{(\mu\nu\rho)(\alpha\beta\gamma)} &= \frac{1}{3} [[P..P..]]_{(\mu\nu\rho)(\alpha\beta\gamma)} \\ &= \begin{vmatrix} P_{\mu\alpha} & P_{\mu\beta} & P_{\mu\gamma} \\ P_{\nu\alpha} & P_{\nu\beta} & P_{\nu\gamma} \\ P_{\rho\alpha} & P_{\rho\beta} & P_{\rho\gamma} \end{vmatrix}, \\ ..P| &= \frac{1}{4} [[P..P..]] = \frac{1}{6} [[P..P..]] \\ &= \begin{vmatrix} P_{11} & P_{12} & P_{13} & P_{14} \\ P_{21} & P_{22} & P_{23} & P_{24} \\ P_{31} & P_{32} & P_{33} & P_{34} \\ P_{41} & P_{42} & P_{43} & P_{44} \end{vmatrix}, \end{aligned} \right\} \text{(xx.)}$$

Now, by interchanging the two groups of suffixes of each of these, writing them with contravariant instead of covariant suffixes, and dividing by  $..|P|$ , we obtain a new series :

$$\left. \begin{aligned} Q^{\mu\alpha} &= \frac{..P_{(\beta\gamma\delta)(\rho\sigma)}}{..|P|}, \\ Q^{(\mu\nu)(\alpha\beta)} &= \frac{..P_{(\gamma\delta)(\rho\sigma)}}{..|P|}, \\ ..Q^{(\mu\nu\rho)(\alpha\beta\gamma)} &= \frac{..P_{\delta\sigma}}{..|P|}, \\ ..Q| &= \frac{1}{..|P|}; \end{aligned} \right\} \text{. . . (xxi.)}$$

and these we find form a sequence of exactly the same kind as the P sequence ; to wit

$$\begin{aligned}
 \cdot Q^{(\mu\nu)(\alpha\beta)} &= \frac{1}{2} [[ \cdot Q \cdot \cdot Q ] ]^{(\mu\nu)(\alpha\beta)} \\
 &= \begin{vmatrix} \cdot Q^{\mu\alpha} & \cdot Q^{\mu\beta} \\ \cdot Q^{\nu\alpha} & \cdot Q^{\nu\beta} \end{vmatrix}, \\
 \cdot\cdot Q^{(\mu\nu\rho)(\alpha\beta\gamma)} &= \frac{1}{3} [[ \cdot Q \cdot \cdot Q \cdot ] ]^{(\mu\nu\rho)(\alpha\beta\gamma)} \\
 &= \begin{vmatrix} \cdot Q^{\mu\alpha} & \cdot Q^{\mu\beta} & \cdot Q^{\mu\gamma} \\ \cdot Q^{\nu\alpha} & \cdot Q^{\nu\beta} & \cdot Q^{\nu\gamma} \\ \cdot Q^{\rho\alpha} & \cdot Q^{\rho\beta} & \cdot Q^{\rho\gamma} \end{vmatrix}, \\
 \cdot\cdot\cdot Q &= \frac{1}{4} [[ \cdot Q \cdot \cdot\cdot Q ] ] = \frac{1}{6} [[ \cdot Q \cdot \cdot Q \cdot ] ] \\
 &= \begin{vmatrix} \cdot Q^{11} & \cdot Q^{12} & \cdot Q^{13} & \cdot Q^{14} \\ \cdot Q^{21} & \cdot Q^{22} & \cdot Q^{23} & \cdot Q^{24} \\ \cdot Q^{31} & \cdot Q^{32} & \cdot Q^{33} & \cdot Q^{34} \\ \cdot Q^{41} & \cdot Q^{42} & \cdot Q^{43} & \cdot Q^{44} \end{vmatrix},
 \end{aligned}
 \tag{xxii.}$$

The relations between these two sets of tensors, considered as linear tensor operators, are important. If for instance,  $\cdot P_{\mu\alpha} \cdot A^\alpha = X_\mu$ ,  $\cdot P_{\mu\alpha} \cdot B^\alpha = Y_\mu$ ,  $\cdot P_{\mu\alpha} \cdot C^\alpha = Z_\mu$ ,  $\cdot P_{\mu\alpha} \cdot D^\alpha = W_\mu$ , then also  $\cdot Q^{\mu\alpha} X_\alpha = A_\mu$ , etc. ; moreover,

$$\cdot P_{(\mu\nu)(\alpha\beta)} [\cdot A \cdot \cdot B]^{(\alpha\beta)} = [\cdot X \cdot \cdot Y]_{(\mu\nu)}$$

and  $\cdot Q^{(\mu\nu)(\alpha\beta)} [\cdot X \cdot \cdot Y]_{(\alpha\beta)} = [\cdot A \cdot \cdot B]^{(\mu\nu)}$ , etc. ;

$$\cdot\cdot P_{(\mu\nu\rho)(\alpha\beta\gamma)} [\cdot A \cdot \cdot B \cdot \cdot C]^{(\alpha\beta\gamma)} = [\cdot X \cdot \cdot Y \cdot \cdot Z]_{(\mu\nu\rho)}$$

and  $\cdot Q^{(\mu\nu\rho)(\alpha\beta\gamma)} [\cdot X \cdot \cdot Y \cdot \cdot Z]_{(\alpha\beta\gamma)} = [\cdot A \cdot \cdot B \cdot \cdot C]^{(\mu\nu\rho)}$ , etc. ;

and  $\cdot\cdot\cdot | P | [\cdot A \cdot \cdot B \cdot \cdot C \cdot \cdot D] = [\cdot X \cdot \cdot Y \cdot \cdot Z \cdot \cdot W]$

$$\cdot\cdot\cdot | Q | [\cdot X \cdot \cdot Y \cdot \cdot Z \cdot \cdot W] = [\cdot A \cdot \cdot B \cdot \cdot C \cdot \cdot D]$$

Each Q-tensor is in fact the reciprocal of the corresponding P-tensor.

In the case of the metric tensor,  $g_{\mu\alpha}$  and  $g^{\mu\alpha}$ , the interchange of the two suffix-groups is inoperative, on account of the symmetry of the tensor. Between  $g_{(\mu\nu)(\alpha\beta)}$  and  $g^{(\rho\sigma)(\gamma\delta)}$  the geometric mean  $g_{(\mu\nu)(\alpha\beta)} = \frac{g_{(\mu\nu)(\alpha\beta)}}{\sqrt{-..|g|}}$  and  $g^{(\rho\sigma)(\gamma\delta)} = \frac{g^{(\rho\sigma)(\gamma\delta)}}{\sqrt{-..|g|}}$  is of importance; its type-number is 0.

### § 5. Applications.

The present discussion affects, of course, every branch and application of the tensor calculus; but some indication of its more striking applications may be of interest. Its chief interest certainly lies in the fact that it re-introduces into electrodynamics that similarity between electric and magnetic phenomena which does not fully appear in the usual tensor statement of the laws; since the tensor  $F_{\mu\nu}$  and the tensor-density  $\mathbf{H}^{\mu\nu}$ , on which Mie's electrodynamics rests, are both linear tensors of type  $-2$ ; the tensor  $F_{\mu\nu\rho} + F_{\mu\rho\mu} + F_{\rho\mu\nu}$  and the vector density  $(\mathbf{H}^{\mu\nu})_\nu$  being derived from them in exactly the same manner, by Grassmann multiplication with the symbolic vector of covariant differentiation—the tensor equivalent of Hamilton's operator, which we may conveniently write  $\nabla_\mu$ . In fact, if  $\phi_\mu$  be the potential, Maxwell's equations become:

$$\left. \begin{aligned} \mathbf{F} &= [\nabla, \phi] \\ \mathbf{K} &= [\nabla, \mathbf{F}] = 0 \text{ identically,} \\ \mathbf{C} &= [\nabla, \mathbf{H}] \\ \epsilon &= [\nabla, \mathbf{C}] = 0 \text{ identically,} \end{aligned} \right\} \quad . \quad (\text{xxiii.})$$

where the vanishing vector-density  $\mathbf{K}^\mu$  has for time and space components the density and conduction flux of "magneticity," and the vanishing invariant density  $\epsilon$  represents the departure from conservation of electricity.

Similarly, if the ponderomotive force be given by the covariant vector-density  $\mathbf{P}_\mu$ , we have

$$\mathbf{P} = [\mathbf{F}, \mathbf{C}], \quad . \quad . \quad . \quad (\text{xxiv.})$$

while the relation between field and induction is given by

$$d \cdot L = \cdot [H \cdot d \cdot F \cdot], \quad . . . \quad (xxv.)$$

where the invariant-density  $L$  is the density of the action-integral ; this leads to the expression for  $P_\mu$  as the divergence of a mixed tensor-density  $E^\nu_\mu$ ,

$$\left. \begin{aligned} \cdot P \cdot &= \cdot [\cdot \nabla \cdot E \cdot] \\ E^\nu_\mu &= \cdot H^{\nu a} \cdot F_{a\mu} + \cdot L \delta^\nu_\mu \end{aligned} \right\} \quad . . \quad (xxvi.)$$

$\delta^\nu_\mu$  being the idemfactor, which has its four components in the principal diagonal each = 1, and the other twelve each = 0.

In empty space

$$\left. \begin{aligned} \cdot L &= \frac{1}{2} g^{(\mu\nu)(\alpha\beta)} \cdot F_{(\mu\nu)} \cdot F_{(\alpha\beta)} \\ &= \frac{1}{2} \cdot [[g^{\cdot\cdot} (\cdot F \cdot \cdot F \cdot)]], \\ \text{so that} \quad \cdot H^{(\mu\nu)} &= g^{(\mu\nu)(\alpha\beta)} \cdot F_{(\alpha\beta)} \\ \text{or} \quad \cdot H \cdot &= \cdot [g^{\cdot\cdot} \cdot F \cdot] \end{aligned} \right\} \quad . . \quad (xxvii.)$$

A further interesting point is the general law that the Grassmann product of  $\cdot \nabla \cdot$  into any linear tensor is the same as if  $\cdot \nabla_\mu \equiv \frac{\partial}{\partial x^\mu}$ , and is consequently independent of the particular metric or affine relationship by which the covariant derivative may be defined.

The simple form assumed by Stokes's theorem is worth noting :—That whatever the operand may be, and whether the operators be applied in open or Grassmann multiplication, if  $d^2 \cdot S \cdot$  be an element of a very small surface, and  $d \cdot \sigma \cdot$  one of its bounding curves, the following operations are equivalent :

$$\int d \cdot \sigma \cdot \equiv \iint [d^2 \cdot S \cdot \cdot \nabla \cdot]$$

If the Grassmann product of each of these into a tensor operand of type  $-1$  be formed, we have

$$\int [d \cdot \sigma \cdot X \cdot] \equiv \iint [d^2 \cdot S \cdot \cdot \nabla \cdot X \cdot],$$

which no longer applies only to very small circuits, since both sides are invariant.

Green's so-called "divergence theorem" is capable of similar treatment.

Enough has now been said to make clear the importance of the concept which we have called the Grassmann product. The many forms in which it can arise in the usual tensor notation make some clear indication of this type of product as such almost a necessity if the tensor analysis is to attain to the clarity and vigour of the old vector analyses, such as that of Gibbs; that indicated here is only intended as a suggestion, but it is hoped that it may serve to bring the point into relief more clearly than has formerly been the case.

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LXXXIX. *On the Seat of the Electromotive Force in the Galvanic Cell.* By J. A. V. BUTLER, M.Sc., University College of Swansea\*.

ONE of the most disputed and discussed questions of the last century has been the seat and origin of the electromotive force of the galvanic cell and its connexion with the Volta P.D. of metals. Of the reality of the latter there is now no doubt. In the nineteenth century the centre of the controversy was whether the Volta P.D. is an intrinsic property of the metals themselves or due to other causes, *e.g.* chemical action between the metals and air at their surfaces at the moment of breaking contact. The earlier arguments have been summarized in the classical report of Lodge†. The upholders of the intrinsic P.D. view, led by Lord Kelvin‡, could point out that the Volta potential was not markedly affected by replacing air by other gases or in the best vacuum obtainable. They differentiated rightly between the true contact P.D. and the comparatively minute Peltier effect. The chemical theorists, whose position was stated most cogently by Sir Oliver Lodge§, were able to adduce the close correspondence between the Volta series and the heats of oxidation of the metals. They held that the true contact P.D. between two metals was merely the equivalent of the Peltier effect. The apparent P.D. in a bath of

\* Communicated by the Author.

† B. A. Reports, Montreal, 1884; *Phil. Mag.* [5] xix. 1835.

‡ *Phil. Mag.* xlv. p. 82 (1898); *Collected Works*, vi. p. 110.

§ *Phil. Mag.* xlix. p. 351 (1900), and *Proc. Phys. Soc. Lond.* xvii. p. 369 (1900).

oxygen or other "oxidizing" medium was due to the differential attraction of the metals for the electro-negative oxygen. In the galvanic cell in which the oxygen was replaced by an aqueous solution, an "oxidizing liquid," a very similar state of affairs was supposed to hold.

The chemical theory of the galvanic cell was greatly strengthened by the discovery in the Gibbs-Helmholtz equation of the exact relation between the energy of the chemical process occurring in the cell and the electrical energy produced. The physico-chemical theory of Nernst, in referring the E.M.F. to processes at the electrodes analogous to solubility, served further to focus attention on these junctions as the main seat of the E.M.F., and the success of this theory in accounting for the effect of concentration and the extensive use of the galvanic cell for determining the maximum work of chemical reactions led for a time to an almost universal belief in its sufficiency.

The investigation of photoelectric phenomena has, however, resulted in the complete establishment of the reality of an intrinsic P.D. between metals of substantially the same magnitude as the measured Volta P.D. The necessity for taking this into account in photoelectric experiments was first recognized by Richardson and Compton\*, and in a series of particularly elegant experiments Millikan and his co-workers† conclusively demonstrated its existence by showing that, provided it is taken into account, the Einstein equation

$$\frac{1}{2}mv^2 = Ve = h\nu - \phi$$

universally holds; further, that the contact P.D. measured under the best conditions‡ closely approximates to the relation:

$$\text{C.P.D.} = \phi_1 - \phi_2 = h(V_1 - V_2),$$

where  $\phi_1$  and  $\phi_2$  are the "electronic work functions," i.e. the amounts of work necessary to remove an electron from the metals, expressed in volts, and  $V_1$ ,  $V_2$  the "threshold frequencies."

We shall regard the existence of a contact P.D. between metals of substantially this magnitude as established. The contact P.D. does in fact differ from the quantity  $\phi_1 - \phi_2$  by an amount corresponding to the Peltier effect. The relation has been discussed in another paper§. But the Peltier

\* Phil. Mag. xxiv. p. 592 (1912).

† Phys. Rev. vii. p. 18 (1916); xviii. p. 236 (1921).

‡ Hennings & Kadesch, Phys. Rev. viii. p. 217 (1916).

§ Phil. Mag. October 1924.

effect never exceeds a few millivolts in magnitude and for present purposes may be neglected.

The bearing of the existence of large metal contact P.D.'s on the theory of the galvanic cell has been discussed at some length by Langmuir §. We shall here pursue a different line of thought.

In Table I. are given some representative values of the electronic work functions of the metals, which are taken

TABLE I.

Metal.	$\phi$ .*	$\phi_e$ †	$\phi_{Pt} - \phi_M$	Heat of solution, kgm. cal.	Heat of solution, volts.	Authority for heat of solution.‡
K .....	1.45	2.92	2.95	45.4	1.97	Mean.
Na .....	1.82	2.71	2.6	43.7	1.89	Mean.
Li .....	2.35	2.96	2.1	51.2	2.22	Mean.
Ca .....	2.57	2.5	1.8	65	2.82	G
Mg .....	2.7	1.49	1.7	55.1	2.39	R
Al .....	3.0	1.34	1.4	42.3	1.83	R
Zn .....	3.4	.76	1.0	18.2	.79	R
Cd ....	3.49	.40	.9	8.6	.37	R
Fe .....	3.7	.44	.7	10.4	.45	R
Sn .....	3.8	.14	.6	2.3	.10	T
Pb .....	3.42	.12	1.0			
Cu .....	4.0	-.34	.4	-8.2	-.36	Ind.
Hg .....	...	-.80	—			
Ag .....	4.1	-.80	.3			
Pt .....	4.4	...	—			

\* Langmuir and Hughes, *loc. cit.*

† Lewis and Randall, 'Thermodynamics,' p. 433, except Ca and Mg from Abegg, Auerbach and Luther, 'Messungen Electromotorischen Kräfte'; Al, Heyrovsky, J. Chem. Soc. cxvii, p. 27 (1920).

‡ Mean = mean of values given in Landolt-Börnstein, 4th edition. G = Guntz, R = Richards, T = Thomson. Value for Cu based on reaction  $\text{CuSO}_4\text{aq} + \text{Fe} = \text{FeSO}_4\text{aq} + \text{Cu} + 37.2 \text{ cal. (T)}$ .

chiefly from a table compiled by Langmuir || from the measurements available (1916) and in a few cases from Hughes ¶. More recent work has not made it possible to

§ Trans. Amer. Electrochem. Soc. xxix, p. 125 (1916).

|| *Loc. cit.*

¶ 'Photoelectricity,' p. 40.

*Phil. Mag.* S. 6. Vol. 48. No. 287. Nov. 1924.

3 Q



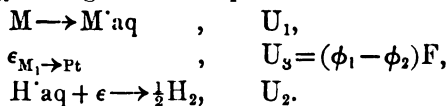
undertake a thorough revision of these data \*. Owing to the extreme sensitiveness of thermionic and photoelectric effects to minute disturbing causes, the values of this important quantity are still barely known. The figures given can hardly be regarded as numerical data, they give merely a general idea of the order of magnitude of the quantity in question and the trend of its variations.

In the third column are the electrolytic normal potentials of the metals measured against the normal hydrogen electrode. The electrode material in this case is platinum and the metal junction that between the metal and platinum. The fourth column gives the values of this metal contact P.D. estimated from the figures in the first column.

The two sets of values exhibit a very marked correspondence, and if the figures in the first column are anything like correct, it must be concluded that the metal contact P.D. is largely responsible for the E.M.F. of the complete cell. The sum of the electrode P.D.'s, which is equal to the difference between the E.M.F. of the whole cell and the metal contact P.D., appears in most cases to be comparatively small.

It is necessary to reconcile this conclusion with the correspondence between the E.M.F. of the cell and the energy of the chemical reaction at the electrodes. This correspondence is illustrated by the last two columns of Table I., which give the heat of reaction (*i. e.*, of solution of the metal with the liberation of hydrogen) per equivalent, expressed in kilogram calories and in volts.

Now in the cell the reaction  $M + H^+aq = M^+aq + \frac{1}{2}H_2$  is located as follows. At the metal electrode the process is simply the passage of metal ions from the metal lattice into the solution. At the metal junction the transfer of electrons from one metal to the other occurs, and at the hydrogen electrode the electrons discharge hydrogen ions, and the hydrogen atoms so formed yield diatomic hydrogen. Let the total energy changes of these processes be as follows †:



\* Some recent determinations may be quoted:—

Roy (Phil. Mag. xlvii. p. 561, 1924): Na 2.15 (T), 2.26 (P); Ca 2.86 (T), 3.34 (P); Pt 4.25 (T), 4.42 (P). Young (Proc. Roy. Soc. A, civ. p. 611): K 1.1 (T), 1.98 (P).

T = thermionic measurements.

P = photoelectric measurements.

† Convention as to sign: U is written positive if the total energy increases in the process, *i. e.* heat absorbed.

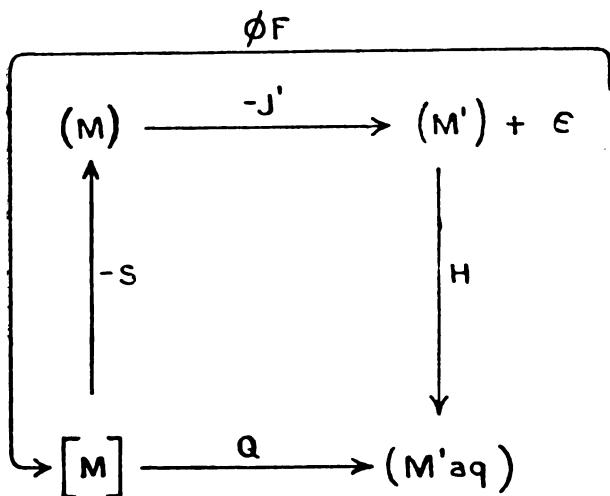
It may be as well to point out that by the "total energy change" at a junction is meant the heat effect when no electrical work is done. In the galvanic cell only a small part of the energy of the reaction is liberated in the cell as heat.

The sum of the total energy changes throughout the cell is equal to the heat of the reaction  $Q$ ; *i. e.*,

$$U = -Q = U_1 + (\phi_1 - \phi_2)F + U_2.$$

The sum of the energy changes at the two electrodes ( $U_1 + U_2$ ) might be got by subtracting the electronic work difference of the metals from the whole heat of the reaction. But a partly independent estimate of the energy change in the passage of metal ions into solution can be obtained according to the following scheme:—

The metal is vapourized (heat absorbed  $S$ ) and the metal vapour thereupon ionized (heat of ionization  $J$ ). The



electrons are returned to the metal (heat evolved  $\phi F$ ) and the metal ions dissolved in water (heat of hydration  $H$ ).

The total energy change in the passage of metal ions from the metal into the solution is evidently

$$Q_1 = H + \phi F - J - S.$$

Table II. gives the data for the calculation of  $Q_1$  for a number of metals.

TABLE II.

	S.	H.	J.	$n\phi F.$	$Q_1 + HCl.$
$K \rightarrow K^+ \dots\dots$	26.9	184	99	33	91
$Na \rightarrow Na^+ \dots\dots$	30	204	117	42	99
$Li \rightarrow Li^+ \dots\dots$	50	237	123.1	54	118
$Ca \rightarrow Ca^{++} \dots\dots$	35	570	411	$2 \times 59$	$\frac{242}{2} = 121$
$Mg \rightarrow Mg^{++} \dots\dots$	50	672	519	$2 \times 62$	$\frac{227}{2} = 113$
$Zn \rightarrow Zn^{++} \dots\dots$	35.8	731	666	$2 \times 78$	$\frac{182}{2} = 91$
$Cd \rightarrow Cd^{++} \dots\dots$	31.2	678	634	$2 \times 80$	$\frac{173}{2} = 87$
$Pb \rightarrow Pb^{++} \dots\dots$	57.4	598	548	$2 \times 79$	$\frac{151}{2} = 76$
$Cu \rightarrow Cu^{++} \dots\dots$	83.4	247	177	$2 \times 92$	$\frac{171}{2} = 86$
$Ag \rightarrow Ag^+ \dots\dots$	63.3	209	173	94	67

The values of J and S are those of Grim\* and are the same as those employed in the calculation of H. The heat of hydration of any single metal ion is not known with any certainty, but the sum of the heats of hydration of the two ions constituting a salt can be easily obtained when the lattice energy and heat of solution are known†. The figures given refer to the chloride and differ from the true heat of hydration by a constant amount per equivalent, namely the heat of hydration of the chloride ion.

Owing to the great uncertainties about the value of  $\phi$  the final figures can only be taken as indicating the general order of magnitude of the effect. It has been estimated, assuming that the absolute P.D. of the normal calomel electrode is +.56, that the heat of hydration of the chloride ion is 77. If this value is approximately correct, it will be seen that the energy of the process occurring at metal electrodes is in most cases comparatively small and not in general greater than the heats of solution of metal salts. It may also be observed that the values show a general trend in the direction of the voltaic series.

No stress can be laid on the figures themselves, but it is evident that from the point of view of the energy changes concerned there is no difficulty in regarding the metal metal P.D. as an important contributor to the E.M.F. of the galvanic cell, and the forces operating at the metal electrode

\* *Zeits. Phys. Chem.* cii. p. 113 (1922).

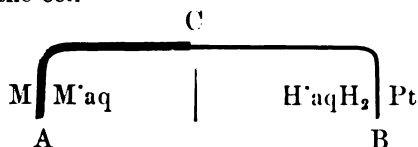
† The heats of hydration are taken from a paper by the author which will appear shortly in *Zeits. Phys. Chem.*

essentially the same as those concerned in the solubility of salts.

It remains to coordinate the statistical expressions for the P.D. at the different types of junctions in such a cell as that which has been considered which have been worked out in previous papers.

*The Statistical Theory of the Galvanic Cell.*

Consider the cell



(1) Metal solution junction A. The passage of metal ions from the metal electrode into the solution is regarded as a process in every respect similar and involving similar forces to those coming into play in the ionic equilibrium between a salt crystal and solution. From this point of view \* it can be shown that the Nernst conception does not involve any physical impossibility such as has been supposed in connexion with the calculated "solution pressures." The following equation is obtained expressing the P.D. at the surface at equilibrium, *i. e.* when metal ions reach and leave the surface at the same rate :—

$$e_1 = \frac{U_1}{nF} + \frac{RT}{nF} \log_e K_1 + \frac{RT}{nF} \log_e C, \quad . . . . (1)$$

where  $K_1$  = a constant determined by the "statistical conditions,"

$C$  = metal ion concentration in the solution.

(2) Hydrogen electrode B. The mechanism of the interchange of electrons between substances in two states of oxidation has also been considered †, and an analogous equation has been deduced :

$$e_2 = - \frac{U_2}{nF} + \frac{RT}{nF} \log_e K_2 + \frac{RT}{nF} \log_e \frac{c_1}{c_2},$$

where  $c_2$  and  $c_1$  are the concentrations of the reduced and oxidized molecules concerned respectively. The case of gas

\* "The Kinetic Interpretation of the Nernst Theory of E.M.F.," Trans. Faraday Soc. xix. p. 729 (1924).

† "A Kinetic Theory of Reversible Oxidation Potentials at Inert Electrodes," Trans. Faraday Soc. xix. p. 734 (1924).

electrodes is rather more complex, involving the dissociation of the diatomic gas, the mechanism of which is obscure. But it is not unreasonable to assume that the relation between the P.D. and the total energy change is of the same form as (2), *i. e.*, we shall write

$$e_2 = -\frac{U_2}{nF} + \frac{RT}{nF} \log_e K_2 + \frac{RT}{nF} \log_e \frac{[H']}{[H_2]^{\frac{1}{2}}}. \quad (2)$$

(3) Metal-metal junction C. Finally an expression has been deduced\* for the P.D. at metal junctions:

$$e_3 = -\frac{U_3}{nF} + \frac{RT}{F} \log_e K_3, \quad (3)$$

where  $U_3 = (\phi_1 - \phi_2)F$ , the total energy change in the passage of electrons from the one metal to the other.

Summing the equations for the P.D.'s at the three junctions we obtain for the E.M.F. of the whole cell

$$E = e_1 - e_2 - e_3 = \frac{U}{nF} + \frac{RT}{nF} \log_e C - \frac{RT}{nF} \log_e \frac{[H']}{[H_2]^{\frac{1}{2}}} + \frac{RT}{nF} \log_e K, \quad (4)$$

which on differentiation gives the Gibbs-Helmholtz equation

$$E - \frac{U}{nF} = T \frac{dE}{dT}.$$

It is thus possible on these lines to reconcile completely the different theories which emerged in the long controversy about the seat of the E.M.F. in the galvanic cell. The "contact" and "chemical" theorists each laid stress on one aspect of the truth, and their conceptions are mutually complementary and in no way inconsistent. The correspondence between the energy of the chemical reaction going on in the cell and the E.M.F. is adequately accounted for, while the Nernst conception of the origin of the E.M.F. remains a fairly accurate representation of the process at soluble metal electrodes.

In conclusion two consequences of this theory may be noted. In the first place the expression (2) for the P.D. of an oxidation-reduction process at an inert electrode involves the electronic work function of the electrode metal†. The

\* Phil. Mag. October 1924.

† Since  $U_2 = (V - \phi)F + H_{M'} - H_M$ , where  $V$  = "ionization potential" of reduced substance in solution,  $H_{M'}$  and  $H_M$  the heats of hydration of the two molecules concerned.

effect of varying the material of the electrode metal on oxidation potentials has not been extensively investigated, although several metals of the platinum group have been employed by various investigators and no difference has been observed. It is evident that when the metal-metal junction is taken into account any variation in the nature of the electrode metal will equally affect the P.D.'s at its two ends. Therefore the E.M.F. of a cell involving a reversible oxidation process at an inert electrode is not dependent on the electrode material\*.

Secondly, in attempts which have been made to determine the absolute P.D.'s at electrodes the possibility of metal contact P.D.'s between the standard and the experimental electrode metals has not been taken into account. By means of different methods involving the preparation of null solutions at mercury electrodes the P.D. of the normal calomel electrode has been located at about +0.56 volt†. On the other hand, using silver powder in the dropping electrode Billitzer‡ found a different value, about +0.1 volt. It has been objected that silver in a finely divided form may not exhibit its true electrolytic P.D., but recently Garrison§, making use of a method to which this objection does not apply, has obtained a result in substantial agreement with Billitzer's. It is suggested that the metal contact P.D. between silver and mercury might account for the discrepancy. Unfortunately, it is not possible at present to estimate this P.D. from the available data with any assurance.

#### Summary.

It is shown that the existence of large metal contact P.D.'s is in no way inconsistent with the correspondence between the E.M.F. of a galvanic cell and the energy of the chemical reaction occurring therein. The statistical expressions deduced in previous papers for the different junctions are coordinated, and a theory of a typical galvanic cell is outlined which includes as different aspects of the whole truth (1) the metal contact P.D. theory, (2) the "chemical" theory, (3) the Nernst theory of metal electrode P.D.'s, (4) the relation between E.M.F. and total energy change expressed in the Gibbs-Helmholtz equation.

\* Experiments to test this deduction are in progress.

† Ostwald and Paschen, *Zeits. Phys. Chem.* i. p. 583 (1887); Palmaar, *ibid.* lix. p. 129 (1907).

‡ *Zeits. Phys. Chem.* xlviii. p. 513 (1904); li. p. 163 (1905). *Zeits. Electrochem.* viii. p. 638 (1902); also Freundlich and Makelt, *Zeits. Electrochem.* xv. p. 161 (1909).

§ J. Amer. Chem. Soc. xlv. p. 37 (1923).

XC. *Contribution to the Kinetic Theory of Vaporization.*  
 By SAMUEL CLEMENT BRADFORD, D.Sc., *The Science Museum, London, S.W.* 7\*.

MODERN research on the electrical structure of matter has confirmed the view of van der Waals that molecules are surrounded by fields of force. And in previous papers † preliminary attempts have been made to study the properties of solutions in relation to molecular attraction, or cohesion pressure, and motion. Strong evidence has been obtained that solution is due to the diminution of the surface energy of the solute by the counter attraction of the solvent, so that a larger number of solute particles have sufficient energy normal to the surface to enable them to overcome the attraction of the solute and escape into the solvent. A general formula was deduced for the force opposing solution, by means of which, the majority of substances can be arranged in the order of their solubility, and, as a necessary consequence, in the order of all the other properties of solutions. For not only do such properties as solubility, degree of hydration, heat of solution, molecular volume, and compressibility follow the order of cohesion pressures, but so also do the depression of the freezing-point, elevation of the boiling-point, diminution of vapour-pressure, and electrical conductivity. It was possible to calculate the effect, on the freezing-point of aqueous salt solutions, of the altered cohesion pressure due to the different field of force of the solute particles; and this effect was found to be the same as the observed increase in the depression below the normal depression caused by the presence of a solute with a cohesion not differing greatly from that of water. This appears to be a possible explanation of the so-called anomaly of the strong electrolytes.

It was pointed out that, if the work done by a particle of solute escaping into solution could be calculated, the critical velocity, normal to the surface, necessary to carry it into the solution could be determined. This supposes that it should be possible to calculate the effects of any redistribution of forces between the molecules of the two kinds in a solution, and to allow for any change in the aggregation of the particles of either kind.

Having deduced an expression for the critical velocity, it should be possible to determine the distribution of particles between the solute and its solution and obtain a formula for

\* Communicated by the Author.

† Phil. Mag. xxxviii. p. 696 (1919); xliv. p. 897 (1922).

the solubility of a given substance in a given solute. This distribution should be of the same nature as the distribution of particles between a liquid and its vapour. However, Dieterici's attempt to deduce a formula for the latter case was unsuccessful, and this simpler equilibrium needs further study before attempting to obtain a formula for solubility. The present paper, therefore, is devoted to the consideration of the vaporization of a liquid.

We will suppose that the liquid, in contact with its vapour only, is maintained within an enclosure at a constant temperature under ordinary laboratory conditions; so that, if heat be abstracted from the liquid by the escaping particles of vapour, it will be supplied immediately from the enclosure, while simultaneously any gain of temperature by the vapour will be compensated.

According to Maxwell's law of the distribution of velocities, the number of particles in unit volume of the liquid that have velocities whose vertical components lie between  $u$  and  $u + du$  is

$$\frac{n_s}{V_{ps} \sqrt{\pi}} e^{-\frac{u^2}{V_{ps}^2}} du, \dots \dots \dots (i)$$

where  $n_s$  is the concentration of liquid particles, and  $V_{ps}$  Maxwell's most probable speed of the particles. The number of particles in unit volume of vapour in the same condition is

$$\frac{n_l}{V_{pl} \sqrt{\pi}} e^{-\frac{u^2}{V_{pl}^2}} du, \dots \dots \dots (ii)$$

$n_l$  being the concentration of the vapour, and  $V_{pl}$  Maxwell's constant for the vapour phase. Therefore, the number of liquid particles per unit volume, having velocities normal to the surface between  $u$  and  $du$ , that strike the surface from below is

$$\frac{n_s}{V_{ps} \sqrt{\pi}} e^{-\frac{u^2}{V_{ps}^2}} u du.$$

But, of all the particles that strike unit area of the surface of the liquid from below, only those that have velocities normal to the surface equal to, or greater than, a certain critical velocity,  $s$ , will be able to escape from the attraction of the liquid and pass into the vapour. The total number of such particles is

$$\int_s^\infty \frac{n_s}{V_{ps} \sqrt{\pi}} e^{-\frac{u^2}{V_{ps}^2}} u du = \frac{n_s V_{ps}}{2 \sqrt{\pi}} e^{-\frac{s^2}{V_{ps}^2}} \dots \dots (iii)$$



Now, the total number of particles from the vapour that strike the same area is, from (ii),

$$\int_0^\infty \frac{n_l}{V_{pl} \sqrt{\pi}} e^{-\frac{u^2}{V_{pl}^2}} u du = \frac{n_l V_{pl}}{2 \sqrt{\pi}}, \quad \dots \quad (\text{iv})$$

and the greater attraction of the liquid phase ensures that all these return to it.

In equilibrium the number of particles escaping from the liquid must be equal to the number returning, so that, from (iii) and (iv),

$$\frac{n_s V_{ps}}{2 \sqrt{\pi}} e^{-\frac{s^2}{V_{ps}^2}} = \frac{n_l V_{pl}}{2 \sqrt{\pi}}$$

or  $n_l = n_s \frac{V_{ps}}{V_{pl}} e^{-\frac{s^2}{V_{ps}^2}} \quad \dots \quad (\text{v})$

It has been assumed that because the particles in a pure liquid are surrounded on all sides by similar particles, the resultant attraction at any point in the interior of a liquid is zero. From which it has been inferred that the average kinetic energy of a particle in a liquid is the same as in the perfectly gaseous state at the same temperature. However, Kleeman\* has shown that this is not the case, because the particles in a liquid do not remain at equal distances apart, and, except when passing through points at which the molecular forces vanish, the particles are under the influence of attraction. Therefore in equation (v) we may not write  $V_{ps} = V_{pl}$ , but

$$V_{ps} = \lambda V_{pl}, \quad \dots \quad (\text{vi})$$

where  $\lambda$  is a factor that will vary with the nature of the substance. Let  $v_l$  be the volume occupied by the number,  $N$ , of molecules in a gramme molecule of the substance in the vapour state, and  $v_s$  the volume of the same number of molecules in the liquid condition, then

$$n_l = \frac{N}{v_l - b_l} \quad \text{and} \quad n_s = \frac{N}{v_s - b_s},$$

where  $b_l$  and  $b_s$  are the apparent volumes of the molecules in either state, defined by Kleeman† as the quantities whose magnitudes affect the external pressure at constant temperature and volume, but not the average velocity of translation of the molecules.

\* *Phi. Mag.* xxiv. p. 101 (1912).

† 'A Kinetic Theory of Gases and Liquids.' New York, 1920.

Equation (v) may then be written

$$v_s - b_s = (v_l - b_l) \lambda e^{-\frac{s^2}{\lambda^2 V_{pl}^2}},$$

or, putting  $v_s - b_s = \Phi_s$  and  $v_l - b_l = \Phi_l$ ,

$$\Phi_l = \Phi_s \lambda e^{-\frac{s^2}{\lambda^2 V_{pl}^2}} \dots \dots \dots \text{(vii)}$$

As a first approximation we may take  $V_{pl}$ , the most probable speed of the particles in the vapour, as equal to  $V_p$ , the most probable speed in a perfect gas, so that

$$V_{pl}^2 = \left( \frac{V}{1.23} \right)^2,$$

where  $V$  is the average kinetic energy velocity in the gaseous state and fulfils the condition that

$$\frac{1}{2} m V^2 = 2.012 \times 10^{-16} T,$$

$m$  being the absolute weight of a particle and  $T$  the absolute temperature.

To determine  $s$  we have

$$\frac{1}{2} m s^2 = W,$$

where  $W$  is the work done by a particle in passing from the liquid into the vapour. From these relations we find that the index of  $e$  in (vii) is

$$\frac{s^2}{\lambda^2 V_{pl}^2} = \frac{7.52 \times 10^{15} W}{\lambda^2 T},$$

and, therefore,

$$\Phi_l = \Phi_s \lambda e^{-\frac{7.52 \times 10^{15} W}{\lambda^2 T}} \dots \dots \dots \text{(viii)}$$

The pressure of the vapour in dynes per sq. cm. is given by the equation

$$p = \frac{V_l}{V} \cdot \frac{RT}{\Phi_l} = 8.315 \times 10^7 \frac{V_l T}{V \Phi_l}, \dots \dots \dots \text{(ix)}$$

where  $V$  is Kleeman's total average velocity of a molecule in the vapour. Again approximately, we may take  $V_l = V$ , so that, from (viii) and (ix), and remembering that 1 atmosphere =  $1.016 \times 10^6$  dynes per sq. cm., the vapour-pressure in atmospheres is

$$p = 81.87 \frac{T}{\lambda \Phi_s} e^{-\frac{7.52 \times 10^{15} W}{\lambda^2 T}} \dots \dots \dots \text{(x)}$$

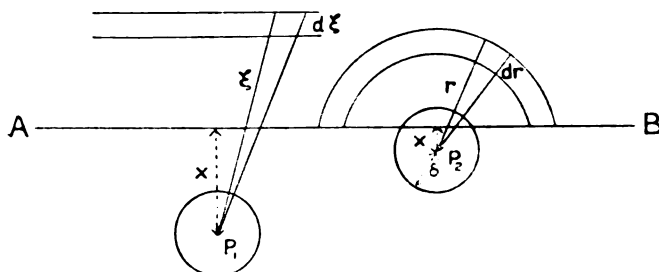
We now have to determine  $W$ , the work done against the

attraction of the liquid by a particle escaping from the liquid into the vapour.

If all the molecules of the liquid are in continual rapid motion, their rotational velocity will insure that a spherical space of diameter  $\delta$  is kept clear around the centre of rotation of each molecule. Two molecules collide when their centres come to a distance  $\delta$  apart\*. Since the molecules are electrically neutral, they will repel in some orientations and attract in others. The attractions will preponderate over the repulsions because the duration of the attractive encounters is greater. If we consider a space element  $dv$  at a definite position relative to a given molecule, the molecules with their centres within  $dv$  will be continually changing their position and attractive forces. In a sufficiently long interval of time, any point within  $dv$  will have been occupied by a molecular centre as often as any other point, and the average value of the force at that point will be the same as at any other point. We are concerned, not with the instantaneous values of the attraction, but only with the average attraction during a reasonably long interval of time. The space element  $dv$  may be situated at any distance from the attracted molecule equal to or greater than  $\delta$ . Edser† has shown that the properties of liquids are explained by the assumption that the average attraction between two molecules whose centres are at a distance  $r$  is

$$f = \frac{c}{r^8},$$

where  $c = \frac{6K\delta^4}{\pi N^2}$ ,  $K$  being the cohesion of the liquid, and  $N$  the number of molecules per unit volume.



In the figure above, let  $P_1$  represent the centre of a molecule

\* Actual collision may not be the rule, and  $\delta$  may be the mean of the nearest distances of the centres during a considerable number of encounters.

† "Molecular Attraction and the Physical Properties of Liquids," Brit. Assoc. 4th Report on Colloid Chemistry, p. 40 (1922).

at a distance  $x$  below the surface AB of the liquid, where  $x > \delta$ . The attraction of the liquid on P may be taken as equal and opposite to the attraction that would be exerted by a continuous mass of liquid above AB. Describe two planes parallel to AB at distances  $\xi$  and  $\xi + d\xi$  above AB. Then the molecules whose centres would lie between these planes would exert on  $P_1$  a resultant attraction equal to

$$\frac{2\pi cN d\xi}{(x + \xi)^6} \int_0^\pi \cos^6 \theta \sin \theta d\theta = \frac{2\pi cN d\xi}{7(x + \xi)^6}.$$

The attraction per unit area exerted on  $P_1$  by all the molecules whose centres would lie above AB would be equal to

$$\frac{2\pi cN}{7} \int_0^\infty \frac{d\xi}{(x + \xi)^6} = \frac{2\pi cN}{35x^5} \quad \dots \quad (\text{xi}).$$

When the distance below AB of the escaping molecule becomes less than  $\delta$ , as at  $P_2$ , the procedure needs to be modified. Around  $P_2$  describe a sphere of radius  $\delta$ ; the section of this sphere above the plane AB will contain no centres of attracting molecules. With  $P_2$  as centre describe spheres with radii  $r$  and  $r + dr$ , where  $r > \delta$ . The resultant attraction by molecules whose centres lie between these spheres is

$$\frac{2\pi cN dr}{r^6} \int_0^{\cos^{-1}(\frac{x}{r})} \cos \theta \sin \theta d\theta = \frac{\pi cN dr}{r^6} \left(1 - \frac{x^2}{r^2}\right),$$

and the total attraction on  $P_2$  by all molecules whose centres would lie above AB is

$$\pi cN \int_\delta^\infty \left(\frac{1}{r^6} - \frac{x^2}{r^8}\right) dr = \pi cN \left\{ \frac{1}{5\delta^5} - \frac{x^2}{7\delta^7} \right\}.$$

The work done by the molecule at P in escaping to the surface of the liquid is, therefore,

$$\frac{2\pi cN}{35} \int_{-\infty}^{-\delta} \frac{dx}{x^5} - \pi cN \int_{-\delta}^0 \left( \frac{1}{5\delta^5} - \frac{x^2}{7\delta^7} \right) dx = \frac{29\pi cN}{210\delta^4}. \quad (\text{xiii}).$$

An equal amount of work must be done in escaping completely from the surface to infinity. So that, neglecting the small attraction of the vapour, the total work done by a particle of liquid passing into the vapour is

$$W = \frac{29\pi cN}{105\delta^4} \quad \dots \quad (\text{xiv}).$$

Making use of the relations

$$c = \frac{6K\delta^4}{\pi N^2} \quad \text{and} \quad N = 6.23 \times 10^{23} \frac{\rho}{M},$$

where  $\rho$  is the density of the liquid and  $M$  its molecular weight, we have

$$W = 2.66 \times 10^{-24} \frac{KM}{\rho},$$

and therefore from (x)

$$p = 81.87 \frac{T}{\lambda \Phi_s} e^{-\frac{2.000 \times 10^{-8} KM}{\lambda^2 \rho T}} \quad \dots \quad (xv)$$

In this formula there is one variable,  $\lambda$ , that is practically unknown. Kleeman has attempted to calculate the ratio of  $V_t$  to  $V_a$  for  $\text{CO}_2$  at 112 atmospheres, and finds it equal to about 1.6. This figure is rather too high for use in the present formula, though probably more accurate analysis would introduce other factors. Moreover, we have to allow for the variation of  $\lambda$  with the nature of the liquid. It is necessary to make an assumption. Accordingly we suppose that, for densities between about 0.6 and 1.0,  $\lambda^2$  is proportional to the density of the liquid, or

$$\lambda^2 = \mu \rho. \quad \dots \quad (xvi.)$$

If  $\mu$  is given the value 2.012, very good agreement of the calculated with the experimental data is obtained.

There is, then, the further difficulty that different methods of calculating  $K$  give values for the same liquid at the same temperature which are altogether incompatible. For instance, the following figures for  $K \times 10^{-9}$  have been found by different workers to three places of decimals:—

Toluene.....	1.554
	2.426
	1.710
	2.210
	3.570
Acetic acid .....	2.977
	1.919
	4.786
	2.100
	5.960
	7.140
Water .....	6.375
	12.450
	3.645
	11.600
	17.300

Since the cohesion occurs exponentially in the formula, it is obvious that such methods of determining  $K$  are useless for the present purpose. Fortunately, however, Edser has obtained a relation between surface tension and cohesion,

$$S = \frac{K\delta}{4},$$

which he has shown to give values of  $S$  as near the experimental results as could be expected, considering the uncertainty attaching to the magnitude of the cohesion. And, if surface tension is indeed the outward expression of the internal molecular forces, it is likely that the cohesion of liquids can be calculated with considerable accuracy from the observed values of their surface tensions. Consequently, in the present paper, the cohesion has been determined from the formula

$$K = \frac{4S}{\delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (xvii)$$

And the figures given in the table at the end confirm the expectation that this is by far the best means known of determining this quantity.

To calculate  $\delta$ , Edser uses the formula

$$\delta = \left( \frac{3.24M}{2.016\rho_m} \right)^{1/3} \times 10^{-8} \text{ cm.},$$

where  $M$  is the molecular weight, and  $\rho_m$  the density near to the freezing-point.

Finally, to reduce the vapour-pressure formula to a form suitable for calculation, the factor  $A$  must be introduced to allow for the molecular aggregation of the liquid. Then by making use of the relations (xvi) and (xvii), and putting

$$V = \frac{M}{\rho} \quad \text{and} \quad \delta' = \delta \times 10^8,$$

we obtain

$$p = 56.47 \frac{T}{\Phi_{\rho}^{1/2} A} e^{-\frac{3.80687 T A^{2/3}}{T \delta \rho}} \quad . \quad . \quad (xviii)$$

In this expression the values of all the variables can be ascertained with tolerable accuracy, excepting those of  $\Phi$ , or  $(v-b)$  and  $A$ . This indicates the need for further research on co-volume and association.

As the former does not occur exponentially, its importance is not so great in the present instance, and it is possible to use a tentative expression for its evaluation, which is

deduced as follows. Kleeman suggests that the apparent molecular volume,  $v_0$ , at absolute zero is a superior limit of the apparent volume,  $b$ , at higher temperatures. He obtains approximate values of  $v_0$  from the coefficient of expansion. For carbon dioxide and benzene he finds  $v_0 = 25.5$  and  $70.6$  c.c. respectively. The corresponding figures for a single molecule are  $v_0' = 41.1 \times 10^{-24}$  and  $114 \times 10^{-24}$  c.c. The following table shows the molecular diameters  $(v_0')^{1/3} \times 10^{-8}$  for these substances as well as for ether and carbon tetrachloride. For comparison, the third column gives Edser's values of  $\delta$ , and the fourth column the ratio  $(v_0')^{1/3} / \delta$ .

Substance.	$(v_0')^{1/3} \times 10^{-8}$ .	$\delta \times 10^{-8}$ .	Ratio.
Carbon dioxide .....	3.44	4.144	.832
Benzene .....	4.84	5.192	.932
Ether .....	4.87	5.277	.925
Carbon tetrachloride .....	4.88	5.313	.920

It will be seen that  $\delta$  is somewhat larger than Kleeman's superior limit of  $b$ , and that the ratio for the three liquid substances is practically constant at 0.926. It is inferred that  $0.926\delta$  is the superior limit of  $b$ . In another place Kleeman makes an estimate of the actual size of  $b$  for carbon dioxide from determinations of  $n$ , the number of molecules crossing a square centimetre from one side to the other in a second, and  $V$ , the total average velocity of a molecule. This second estimate is likely to be more accurate than the former. For carbon dioxide at  $0^\circ$  he finds  $b = 12.2$  c.c. instead of 25.5 as determined from the coefficient of expansion. It is probable, therefore, that 0.926 is about twice the true volume of  $b$  for a single molecule, or for a gramme molecule

$$b = \frac{1}{2}(0.926\delta)^3 \times 10^{-24} \times 6.23 \times 10^{23} \\ = 0.248\delta^3.$$

It does not seem possible yet to allow for change of  $b$  with temperature. In the present paper, therefore, the co-volume is taken as

$$\Phi = v - \frac{\delta^3}{4} \dots \dots \dots \text{(xix)}$$

Although some modification will be necessary in the light of greater knowledge of the nature of liquids and more capable analysis, it seems probable that the mechanism of vaporization is very much as has been suggested above. On applying the formula (xviii) to substances such as ether, *n*-hexane, and *p*-xylene, which are practically unassociated and for which *A* is therefore nearly unity, values for the vapour-pressure at any temperature are obtained which agree extraordinarily well with the experimental figures and become equal to one atmosphere at the boiling-point, as shown in columns eleven and twelve of the table which follows. If the calculated and observed vapour-pressures differ, association is indicated. Unfortunately, again, molecular aggregation has been studied very little. Most methods of calculating association have slight theoretical basis, and the various processes give values differing by fifty or a hundred per cent. Since the present formula is particularly sensitive to slight differences in association, the expression may be used as a means of calculating *A*. This has been done in the table. It will be seen that the values given in column nine differ very little from those calculated by Ramsay and Shields\*, or Traube†, which are added in column ten for comparison. For instance, Ramsay and Shields's figure, 1.05, for benzene corresponds to a vapour-pressure of 82 mm. instead of 74, as observed by Young and Regnault, which requires *A* to be equal to 1.065. This agreement is further confirmation of the truth of the vapour-pressure formula. It may be noted that the figures obtained by Ramsay and Shields were modified subsequently, but it is probable that the earlier values are nearer the truth. The theory will be of use in calculating the effects of the cohesions of salts on the vapour-pressures of their solutions. And it will be possible to ascertain whether the observed increases in the diminution of the vapour-pressure or elevation of the boiling-point, like the increases in the depression of the freezing-point, beyond those due to a neutral solute, are due merely to the cohesions of the salt particles being greater than that of the solvent.

The data for the surface-tensions and densities were taken where possible from Jaeger's‡ results; the other figures from the new edition of Landolt and Börnstein's *Tabellen*. The higher temperatures given in the third column of the table are the boiling-points of the respective liquids; the densities at these temperatures were extrapolated from Jaeger's data. The rather low boiling-point quoted for toluene suggests that this substance was slightly impure or moist.

\* J. C. S. lxiii. p. 1089 (1893).

† Ber. xxx. p. 265 (1897).

‡ Zeitsch. anorg. Chemie, ci. p. 1 (1917).



Substance.	Molecular weight M.	Temperature Centigrade.	Density $\rho$ .	Molecular volume V.	$\delta'$ .	Co-volume $\Phi$ .	Surface-tension S.	Association calculated		Vapour-pressure.		
								from vapour-pressure.	by other methods.	Calculated.	Observed.	
											Atmo-spheres.	mm.
Ether .....	74.08	34.8 20.5	.698 .758	106.13 97.73	5.277 5.277	69.39 60.99	15.9 21.5	1.00 1.00		1.04	1.00	c. 68 120
n-Hexane ...	86.12	20	.660	130.6	5.905	79.10	17.41	1.00				
p-Xylene ..	106.08	136.2 25.7	.757 .857	140.13 123.68	5.555 5.555	97.28 80.83	18.1 29.1	1.00 1.00		1.00	1.00	—
Toluene .....	92.06	109.4 26	.780 .860	111.13 107.05	5.383 5.383	79.12 68.06	19.5 28.4	1.00 1.00		1.32	1.00	48
Benzene .....	78.05	80.5 20	.810 .878	96.36 88.90	4.946 4.946	66.09 58.63	20.7 28.7	1.065 1.065	1.05 R & S	1.00	1.00	75
Acetone ....	58.05	53 20	.710 .778	81.76 74.61	4.618 4.618	57.14 49.99	19.4 21.9	1.05 1.27	1.26 R & S	1.02	1.00	179
Ethyl acetate	88.06	77.1 25.1	.816 .893	107.9 98.61	5.360 5.360	69.4 60.12	17.2 22.2	1.00 1.43		0.95	1.00	95
Pyridine.....	79.05	114.5	.882	89.73	4.911	63.12	25.2	1.18		1.00	1.00	
Aniline .....	93.04	184 43.1	.867 1.000	107.80 93.04	5.253 5.253	71.60 56.80	24.3 40.8	1.30 1.60	1.35 T	0.99	1.00	1
Alcohol .....	46.05	78.4 25	.737 .786	62.48 58.59	4.641 4.641	37.49 33.60	17.0 21.3	2.17 2.46	2.43 R & S	1.01	1.00	59
Water .....	18.02	100 20	.958 .998	18.80 18.06	3.079 3.079	11.50 10.76	58.92 70.6	2.30 2.60	2.66 R & S 3.44 R & S	1.01	1.00	17

## Summary.

The kinetic theory has been applied to obtain a quantitative expression for the vapour-pressure of liquids in the form

$$p = 56 \cdot 47 \frac{T}{\Phi \rho^{1/2} A} e^{-\frac{3 \cdot 806 S V A^2}{T \delta' \rho}},$$

where

$T$  is the absolute temperature,

$\Phi$  the co-volume,

$\rho$  the density,

$A$  the degree of association,

$S$  the surface-tension,

$V$  the volume of a gramme molecule, and

$\delta' \times 10^8$  the nearest distance of approach of the centres of two molecules of the liquid.

Vapour-pressures calculated by means of the formula agree very well with the values observed at given temperatures, and become equal to an atmosphere at the boiling-points of the liquids.

Edser's formula  $S = \frac{K\delta}{4}$  may be used to calculate the cohesion of liquids with considerable accuracy.

XCI. *Investigations on the Latent Photographic Image.*—

Part I. *The Relation between the Light Frequency and Number of Developable Centres.* By F. C. TOY, D.Sc., F.Inst.P., and H. A. EDGERTON\*.

(Communication No. 39 from the British Photographic Research Association Laboratories.)

THE relation between the number of developable centres ( $n$ ) in a photographic emulsion and the wave-length ( $\lambda$ ) or frequency ( $\nu$ ) of the light which produces them is one of the most important problems in the development of photographic theory. Not many attempts have yet been made along this line. The relationships between  $n$  and  $\lambda$  which are vital to the light dart theory as developed by Silberstein (Phil. Mag. *xliii* p. 257, *xliv* p. 956, 1922; *xlv* p. 1062, 1923) have been shown definitely not to hold (Trans. Faraday Soc. *xix* p. 290, 1923). The experimental values of  $n$  at different values of  $\lambda$  and at constant intensity, all

\* Communicated by Dr. T. Slater Price, O.B.E., D.Sc., F.R.S.

other factors being constant, have been shown to be widely different from those which the light dart theory demands, and it seems that the latter can no longer be seriously considered as a basis for theoretical considerations.

In a paper read before the Faraday Society (*ibid.*) it was suggested by one of us that the true relation between  $n$  and  $\lambda$  could not be established without a consideration of the quantity of energy which is *absorbed* by the silver halide itself; especially is this so in view of the fact that the light absorption by the silver halides varies enormously with the frequency. Consider for a moment a given intensity of radiation falling on the silver halide grains. Under certain fixed conditions a given number of centres is produced. Now, if the frequency of the radiation is changed without changing anything else, the alteration in the number of centres produced may be due to two causes:—

(1) It is certainly due mainly to the great change in the quantity of energy available for their formation (*i. e.* the amount absorbed).

(2) It may also be due to the change in frequency, *as such*, which would be expected on the quantum hypothesis.

The object of this investigation is to determine whether the observed relation between the frequency and number of centres produced (with incident intensity and all other variables constant) can be explained by these two factors.

The first problem, then, is to find what fraction of the total amount of incident energy of different frequencies is absorbed by the grains when equal intensity of each light is incident on the surface of the single layer photographic plate. This can be calculated, at any rate approximately, since the refractive indices and extinction coefficients of the gelatin and silver halide crystal are known. The problem divides itself into two parts.—

(a) The determination of the reflexion and absorption losses due to the gelatin.

(b) The reflexion from, and absorption by, the silver halide grains.

We shall consider in this paper only the case of a pure silver bromide emulsion (*i. e.* one containing silver bromide as the only silver halide) with uniform flat grains. The radiations which will be used are the blue, violet, and ultra-violet lines of the mercury arc, with mean wave-length 4358, 4062, and 3650 Å.U. For simplicity all quantities relating

to  $\lambda=4358$  will be denoted by suffix 1, those relating to  $\lambda=4062$  by suffix 2, and those relating to  $\lambda=3650$  by suffix 3. The crystals are assumed to be large enough for the ordinary laws of reflexion and refraction largely to hold.

(a) *Reflexion from and Absorption by Gelatin.*

Let the intensity of all wave-lengths incident at the surface of the gelatin be  $I_0$ . The fraction reflected from the surface may then be taken as given by

$$\frac{(\mu-1)^2 + K}{(\mu+1)^2 + K}, \quad \dots \dots \dots (1)$$

where  $\mu$  = refractive index from air to gelatin, and  $K$  = specific absorption-coefficient of the gelatin. The fraction transmitted is given by

$$4\mu/[(\mu+1)^2 + K]. \quad \dots \dots \dots (2)$$

For the gelatin used, the absorption from  $\lambda=3600$  Å.U. into the visible region was very small; at least it was small enough for any differences in the amounts transmitted to be neglected in our experiments. (This was proved by exposing single-layer plates behind different thicknesses of gelatin and finding no difference in the photographic effect.) The fraction of the incident intensity transmitted through the gelatin layer is therefore

$$4\mu/(\mu+1)^2. \quad \dots \dots \dots (3)$$

In order, therefore, to ascertain the relative transmissions through the gelatin, we have to determine the values of  $\mu$  for the three wave-lengths which are used. An approximate determination of this was carried out as follows:—A piece of dry gelatin was taken, and at a certain point on it fine lines were made on both surfaces. The apparent distance between these was then determined for the mercury lines in the yellow, green, blue-green, blue, and violet, using a 1/12 oil-immersion objective. If the apparent relative distances at wave-lengths  $\lambda_1 \lambda_2$  etc. are denoted by  $a_1 a_2$  etc., then the relative refractive indices are given by

$$\mu_1 : \mu_2 \dots : 1/a_1 : 1/a_2 \dots$$

(Chapman Jones has shown (*Phot. Journ.* li. p. 163, 1911) that the refractive index of air-dried gelatin for yellow light (sodium) is 1.53. Taking this as a starting-point and using the relative values obtained as above, the actual values of the refractive index at different wave-lengths were obtained.

These were plotted on a graph, and the value for the ultra-violet line found by extrapolation, a procedure which is justified since this wave-length is still remote from the position of the ultra-violet absorption band of gelatin. From this curve we get for the three values of the refractive index which we require

$$\mu_1 = 1.539, \quad \mu_2 = 1.543, \quad \mu_3 = 1.549.$$

Applying these values to equation (3), we obtain for the intensities transmitted through the gelatin on to the crystal face :

$$\left. \begin{array}{l} \text{blue} \quad \quad \quad = 0.955 I_0 \\ \text{violet} \quad \quad = 0.954 I_0 \\ \text{ultra-violet} = 0.953 I_0 \end{array} \right\}, \quad . \quad . \quad . \quad (4)$$

and these may be regarded as equal to well within the accuracy possible or required.

*If, therefore, equal intensities are incident on the plate surface, approximately equal intensities will also be incident on the face of the crystals.*

(b) *Reflexion from Crystal Surface and Absorption by Crystal.*

To determine this we must know the refractive index of silver bromide relative to air. This has been determined by Wernicke (Pogg. Ann. cxxxix. p. 132, 1870). Plotting a curve of  $\mu$  against  $\lambda$ , and proceeding in the same way as before, we obtain the following values :

$$\mu_1 = 2.35, \quad \mu_2 = 2.40, \quad \mu_3 = 2.48,$$

from which, with the values given above for gelatin, the following values for the refractive index from gelatin to silver bromide are obtained :

$$\mu_1 = 1.35, \quad \mu_2 = 1.55, \quad \mu_3 = 1.60.$$

Now, since the silver bromide absorbs all the lights used very strongly, equation (3) cannot be applied to finding the intensities just inside the crystal face without first determining whether  $K$  may be neglected or not.

The absorption of silver bromide has been determined by Slade and Toy (Proc. Roy. Soc. A, xcvi. pp. 181-190, 1920), who give the values of  $k$  in the equation

$$I_2 = I_1 e^{-kd},$$

where  $I_1$  and  $I_2$  are the intensities at two points  $d$  cm. apart

in the silver bromide. The values given are :

$$k_1 = 4.86 \times 10^2, \quad k_2 = 16.28 \times 10^2, \quad k_3 = 59.0 \times 10^2.$$

K and  $k$  are connected by the relation

$$K = k\lambda/4\pi,$$

whence by calculation  $K_1 = 0.0017$ ,  $K_2 = 0.0053$ ,  $K_3 = 0.0172$ . Even in this case  $K$  is negligible, the value of the fraction of ultra-violet transmitted with  $K$  included being only 0.2 per cent. less than the value calculated if  $K$  is neglected. The fractions transmitted through the upper face of the crystal are :

blue 0.956,      violet 0.953,      ultra-violet 0.945,

so that combining these with (4), we get as the intensities just inside the crystal face ( $I'$ ), in terms of the incident intensities  $I_0$  :

$$\begin{aligned} \text{blue} & \quad (0.955 \times 0.956) \times I_0, \\ \text{violet} & \quad (0.954 \times 0.953) \times I_0, \\ \text{ultra-violet} & \quad (0.953 \times 0.945) \times I_0; \end{aligned}$$

that is,

$$I_1' = 0.912 \cdot I_0, \quad I_2' = 0.909 \cdot I_0, \quad I_3' = 0.901 \cdot I_0. \quad (5)$$

#### *Absorption by the Crystal.*

The energy absorbed by a crystal of thickness  $d$  cm. on the passage through it of light of wave-length  $\lambda$  and extinction coefficient  $k$  is given by

$$I'(1 - e^{-kd}), \quad \dots \dots \dots (6)$$

where  $I'$  is the intensity when  $d=0$  (i.e. just inside the upper face of the crystal). The expansion of this may be written :

$$I' \cdot kd \left[ 1 - \frac{kd}{2!} + \frac{k^2 d^2}{3!} - \dots \right]. \quad \dots \dots \dots (7)$$

Now, according to Sheppard ('Photography as a Scientific Instrument,' p. 133), the thickness of flat crystals in a photographic emulsion is usually not more than 1/14 of their diameter. The crystals used in the experiments to be described were less than  $1\mu$  in linear dimensions, so that we may take an upper limit for  $d$  of about  $0.1\mu$ . This gives a maximum value for  $kd$  (taking  $k$  for ultra-violet) of  $5.9 \times 10^3 \times 0.1 \times 10^{-4}$ ,  $= 0.06$  (approx.). Retaining only two terms in (7) therefore gives an accuracy greater than 1 per cent. at all wave-lengths. With sufficient accuracy

we may therefore put the energy absorbed by the crystal per sec. equal to

$$I' \cdot \frac{kd}{2} (2 - kd). \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If we consider  $I'$  the same for each light used, as they are to within about 1 per cent. (equation (5)), then the relative quantities of energy ( $E$ ) of different wave-lengths absorbed by the grain are as follows :

$$\left. \begin{aligned} E_2/E_1 &= k_2(2 - k_2d)/k_1(2 - k_1d), \\ E_3/E_2 &= k_3(2 - k_3d)/k_2(2 - k_2d). \end{aligned} \right\} . \quad . \quad . \quad (9)$$

In considering what value to give to  $d$ , it must be remembered that the developable centres are, in all probability, formed on the surface of the grain, and it is unlikely that the absorption of energy by atoms in the interior of the crystal has any effect on the latent image formation (a thickness of  $0.1 \mu$  corresponds to about 300 layers of atoms). It is therefore improbable that  $d$  should be taken as anything like the whole thickness of the grain ; rather is it probable that the absorption only by two extremely thin layers at the grain surfaces should be considered. But fortunately the exact value of  $d$  is immaterial, for since  $kd$  is small compared with 2, the values of  $E_2/E_1$  and  $E_3/E_2$  change very little with large changes in  $d$ . Thus, if we assume  $d$  so small that  $kd$  is negligible compared with 2, we get

$$E_1 : E_2 : E_3 :: 1 : 3.35 : 12.1,$$

while, if we put  $d = 0.06 \mu$ , we get

$$E_1 : E_2 : E_3 :: 1 : 3.35 : 11.9 ;$$

and the difference between these is negligible considering the approximate nature of the calculation. Taking as a sufficiently accurate ratio

$$E_1 : E_2 : E_3 :: 1 : 3.35 : 12.0,$$

we get

$$E_2/E_1 = 3.35 \quad \text{and} \quad E_3/E_2 = 3.59. \quad . \quad . \quad (10)$$

These values are calculated on the assumption that the unit of energy is the same in each case—that is, for each frequency. But on the quantum hypothesis it is to be expected that the effectiveness of  $E$ , as regards the formation of centres, depends on the number of quanta it contains and not on the total energy. The ratio of the number of quanta

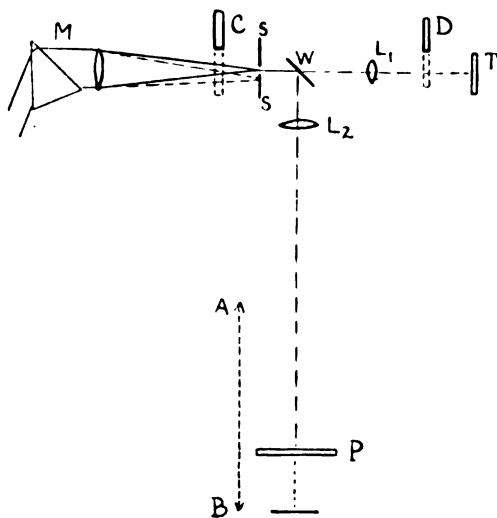
absorbed ( $q$ ) for equal times of exposure is given by

$$\begin{aligned} q_1 : q_2 : q_3 &:: 1 : 3.35 \times \nu_1/\nu_2 : 12.0 \times \nu_1/\nu_3; \\ \text{i. e.} \quad &:: 1 : 3.12 : 10.1 \\ \text{or} \quad &q_2/q_1 = 3.12 \quad \text{and} \quad q_3/q_2 = 3.24. \quad . . . (11) \end{aligned}$$

The object of the experiments now to be described is to determine whether there is any similarity between these figures and the relative number of developable centres produced.

### Experimental.

Light through the monochromatic illuminator, indicated by the prism and lens at M in the figure, is brought to a



focus at the slit SS. After passing through this slit, the light falls on a parallel plate of fused silica W, which is placed at  $45^\circ$  to the direction of the beam. Part of the latter is reflected through the quartz lens  $L_2$ , and forms a very much enlarged image of the face of the prism at P; the other part of the beam, after passing through the quartz lens  $L_1$ , forms a very much diminished image of the prism face at T. C and D are shutters, C placed so that all the light can be cut off, and D so that the light reaching T can be cut off without interfering with continuous illumination of P. In the concentrated light at T is placed a Hilger linear thermopile, connected with a suitable moving-coil galvanometer, and at P are placed the single layer photographic plates



used in the experiments. The whole of the apparatus as shown in the figure (except the prism) is movable about the prism as centre, and by this movement any desired colour can be passed through the slit SS. The special carrier for the plates P is movable between the two points A and B, the reason for this being explained in a moment.

Knowing the intensities incident on the thermopile, the intensities in the other beam must be adjustable so that equal intensities of each light shall be incident on the plate. The first step is to find the relation between the intensity of the light measured by the thermopile and the part reflected from the silica plate and used photographically.

Let the total amount of light falling per second on the silica plate =  $E$  and the fraction transmitted =  $\alpha$ . Then the amount transmitted is  $\alpha E$ , and this falls on the quartz lens  $L_1$ , which transmits a fraction  $\beta$  of it, and therefore an amount  $\alpha\beta E$ , part of which is measured by the thermopile. Since the absorption by the silica plate is negligible, the amount reflected is

$$E(1-\alpha),$$

and this is incident upon a quartz lens  $L_2$ , the transmission of which is practically identical with that of  $L_1$ . Therefore the amount of light in the beam which is active photographically is

$$\beta E(1-\alpha).$$

If the size of the image formed at T is  $a_1$ , then the intensity measured by the thermopile ( $I_t$ ) is given by

$$I_t = \alpha\beta E/a_1.$$

Similarly, the intensity on the plate P ( $I_p$ ) is

$$I_p = \beta E(1-\alpha)/a_2,$$

where  $a_2$  = size of image at P.

Therefore the ratio  $I_p/I_t$  is

$$I_p/I_t = \left(\frac{1-\alpha}{\alpha}\right) \cdot \frac{a_1}{a_2} \quad \dots \quad (12)$$

By means of this we can find the intensity incident on the plate if the intensity on the thermopile be known.

The next thing is to find how  $\alpha$  and the ratio  $a_1/a_2$  vary with the frequency of the light. That very little change of  $\alpha$  with  $\nu$  is to be expected can be shown by calculating the approximate values of  $\alpha$  from the theoretical equation

$$F = \frac{1}{2} \cdot \frac{\sin^2(i-r)}{\sin^2(i+r)} \left[ 1 + \frac{\cos^2(i+r)}{\cos^2(i-r)} \right],$$

where  $F$  = fraction of incident light reflected at a single

surface, and  $i$  and  $r$  are the angles of incidence and refraction respectively. Taking the angle of incidence on the first surface of the silica as  $45^\circ$  (which was only approximate), a value of  $\alpha_1=0.910$  was obtained for the blue, and  $\alpha_2=0.908$  for the ultra-violet. The experimental values were then found directly by measuring the deflexion of the thermopile with and without the silica in position, and the following values found :—

$$\alpha_1=0.903, \quad \alpha_2=0.901, \quad \alpha_3=0.896.$$

It is sufficiently accurate to take these all as equal to 0.900 for our present purpose, so that the value of  $(1-\alpha)/\alpha$  in (12) may be taken as 0.111.

The thermopile was fixed in position as nearly as possible at the focus of the violet light, so that, since the lenses are uncorrected, the blue and ultra-violet were slightly out of focus; but the want of focus was so small that the edges of the image, area  $a_1$ , when photographed appeared almost equally sharp to the eye in each case, and its actual dimensions could be very accurately measured. Similarly, with the enlarged image, area  $a_2$ , formed on the photographic plate. The following values of  $a_1/a_2$  were found :

$$[a_1/a_2]_1=3.91 \times 10^{-3},$$

$$[a_1/a_2]_2=3.77 \times 10^{-3},$$

$$[a_1/a_2]_3=3.75 \times 10^{-3}.$$

The violet and ultra-violet values may be taken as each equal to  $3.76 \times 10^{-3}$ , so that we get finally for the relation between the intensity on the thermopile and on the plate

$$\left. \begin{aligned} [I_p/I_t]_1 &= 3.91 \times 10^{-3} \times 0.111 = 4.34 \times 10^{-4}, \\ [I_p/I_t]_2 &= [I_p/I_t]_3 = 3.76 \times 10^{-3} \times 0.111 = 4.17 \times 10^{-4}. \end{aligned} \right\} \quad (13)$$

Now the intensities of the blue, violet, and ultra-violet on the thermopile were not all equal, but were approximately in the ratio 2 : 1 : 1.2, so that, from (13), the ratios which exist at P, on the photographic plate, can be calculated. But what we require is *equal* intensity on the plate, and this is obtained in the following way. As has been said, P is movable between two points A and B, the size of the image of the prism face depending on the position of P. For only one of these positions is the image strictly in focus, but the depth of focus is so large that the image appeared fairly sharply defined at all points between A and B. Thus, by moving P we have a means of varying the intensity on the plate without

altering the total energy in either beam. After exposure of the plate to the blue, in order to make the violet intensity equal to the blue, on the plate, the latter is moved towards A until the area of the patch of light is reduced in the required proportion. Similarly for the ultra-violet.

In order to test whether this method was accurate, the following experiments were carried out, using only one light. With the plate placed at B, an exposure was made and the thermopile deflexion noted. The intensity of the beam passing through the monochromatic illuminator was then cut down by placing a neutral wedge across the original slit, the wedge being adjusted so that the thermopile deflexion was reduced about half—that is, the intensity at B was reduced to half also. The plate was then moved towards A until the area of the image of the prism face formed on the plate was reduced in such a ratio that the intensity should be the same as it was originally at B. Another portion of the plate was now exposed for the same time. On counting the percentage changed, it was found to be the same at both positions of the plate, thus showing that the method adopted was sound.

To get the absolute values of the intensities, the thermopile was standardized by means of a Hefner lamp. According to Coblentz (Bull. Bur. Standards, xi. p. 89, 1915), if a diaphragm  $14 \times 50$  cm. is placed in front of the Hefner flame at a distance of 10 cm., the intensity of total radiation at a distance of 1 metre from the flame is  $23.2 \times 10^{-6}$  calorie per square centimetre per second. This radiation produced on the galvanometer a deflexion of 45.0 mm.; and since it was known that over the range used the deflexion was strictly proportional to the intensity, it was very easy to interpret all deflexions in absolute intensities.

The single-layer plates used were  $4\frac{1}{2}$  in. long  $\times$  1 in. wide, and by means of a special plate-holder small patches about  $1 \times 0.75$  cm. were exposed along the centre. The plates were developed for 1.5 minutes in amidol developer consisting of 0.4 gm. amidol, 6 c.c. of 10 per cent. KBr, 100 c.c. saturated  $\text{Na}_2\text{SO}_3$ .

The percentage of the grains changed was determined by direct microscopic counting, the average number of developable centres per grain ( $n$ ) being calculated from the equation

$$n = \log_e 100 / (100 - x),$$

where  $x$  is the percentage of grains developed. To obtain a very accurate value of  $x$ , about 1500 grains were counted in every case. The emulsions used varied greatly in speed, but were all *extremely slow*, even compared with the ordinary

process type of emulsion. This is a very important point, the significance of which will be discussed later.

TABLE I.

Blue and Violet only.

Plate Reference No.	Time of Exposure in minutes.	Intensity of light falling on plate in calories per sq. cm. per second.	Average No. centres per grain (obs.).		$n_2/n_1$ (obs.).	$n_2/n_1$ (calc.).
			$n_1$	$n_2$		
E 6 (viii).....	6	$5.25 \times 10^{-9}$	0.043	0.326	7.59	3.12
E 6 (x) .....	15	4.19 „	0.089	0.419	6.14	
E 9 (x) .....	5	4.06 „	0.135	0.683	5.06	
E 15 (v) .....	10	4.58 „	0.301	0.938	3.12*	
E 16 (ii) .....	10	4.25 „	0.281	1.098	3.92	
E 9 (iv) .....	7	4.19 „	0.318	1.195	3.77	
E 9 (ii) .....	6	4.49 „	0.358	1.338	3.74	
E 9 (vi) .....	10	4.19 „	0.344	1.386	4.03*	
E 9 (iii) .....	8	4.32 „	0.532	1.580	2.98*	
E 15 (i) .....	25	4.04 „	0.468	1.690	3.61	
E 9 (v) .....	10	4.27 „	0.533	1.735	3.26	
E 9 (ix) .....	15	4.35 „	0.591	1.815	3.07	
E 15 (vi) .....	35	4.04 „	0.655	2.048	3.14	
E 15 (iii) .....	35	4.18 „	0.710	2.104	2.98	
E 15 (iv) .....	30	4.58 „	0.862	2.440	2.83	

\* Irregular, probably due to some experimental error.

TABLE II.

Violet and Ultra-Violet only.

Plate Reference No.	Time of Exposure in minutes.	Intensity of light falling on plate in calories per sq. cm. per second.	Average No. centres per grain (obs.).		$n_3/n_2$ (obs.).	$n_3/n_2$ (calc.).
			$n_2$	$n_3$		
E 6 (viii).....	8	$4.52 \times 10^{-9}$	0.066	0.431	6.53	3.24
E 16 (i) .....	6	4.10 „	0.103	0.623	6.03	
E 6 (xii) .....	20	4.34 „	0.187	1.120	5.99	
E 6 (vii) .....	6	5.25 „	0.328	1.190	3.63	
E 6 (x) .....	15	4.19 „	0.419	1.370	3.27	
E 15 (vii) .....	8	4.34 „	0.821	2.640	3.21	
E 15 (v) .....	10	4.58 „	0.938	2.990	3.20	
E 6 (ix) .....	20	5.04 „	0.942	3.060	3.25	
E 16 (ii) .....	10	4.25 „	1.098	3.550	3.23	

All the experimental data obtained so far are given in the tables. Table I. gives the results for the blue and violet, and Table II. those for the violet and ultra-violet. The first column merely gives the reference numbers of the emulsion used, column 2 the time of exposure in minutes, column 3 the light intensity in calories per square cm. per second falling on the gelatin surface of the plate. Columns 4 and 5 give the observed average number of centres per grain, obtained as shown above, and column 6 the calculated ratio of the number of centres formed, on the assumption that this is proportional to the number of quanta absorbed (equation 11). Now the first thing to notice about these figures is that when the photographic effect (number of centres) is small, the ratios  $n_2/n_1$  and  $n_3/n_2$  are both large, and that as the effect increases, these ratios decrease and tend to become constant at values of  $n$  greater than about 0.4 for the less effective light of the pair, *i.e.* about 33 per cent. of the grains changed. The constant value of the ratio can be obtained in each case by taking the average of the last five ratios given, as can be seen by inspection of the tables. On comparing these constant ratios with the relative number of quanta absorbed (see equation 11), we see at once that the agreement is good; in the case of the violet-ultra-violet the agreement between  $n_3/n_2$  and  $q_3/q_2$  is almost perfect. For convenience these results are given in summarized form below:—

(a) *Blue, Violet.—Equal incident intensity and time of exposure.*

Relative no. of quanta absorbed  $= q_2/q_1 = 3.12$

Relative no. of centres produced (if  $n_1 > 0.5$ )  $= n_2/n_1 = 3.06$

(b) *Violet, Ultra-violet.—Equal incident intensity and time of exposure.*

Relative no. of quanta absorbed  $= q_3'/q_2 = 3.24$

Relative no. of centres produced (if  $n_2 > 0.4$ )  $= n_3/n_2 = 3.23$

Now these results fit in extremely well with the recent very important work of Eggert and Noddack on the "Proof of the Law of Photochemical Equivalence and the Dry Plate" (*Z. Physik*, xx. p. 299, 1923). They consider that they have proved conclusively that this law holds, and their experiments are certainly very strong evidence in its favour.

There are two important differences between the methods used by Eggert and Noddack and by us :—

(a) They used ordinary thick plates, containing many layers of grains, and found experimentally the absorption by the total silver bromide. The values finally obtained for the same three wave-lengths as we have used were very nearly equal, whereas in our case the absorption of the ultra-violet is about twelve times that of the blue. This is because the effective thickness of silver bromide through which the light passed was very much greater in the plates used by Eggert and Noddack than in our single layer plates, and as  $d$  increases,  $E_2/E_1$  and  $E_3/E_2$  do decrease towards unity, *i. e.*  $E_1$ ,  $E_2$ , and  $E_3$  become more nearly equal as the thickness of silver bromide increases.

(b) They measured what was the “print out” effect, and did not use a developer.

The main conclusions at which they arrived are these :—

- (1) The primary elementary process (in the formation of the latent image) consists in the absorption of one quantum of energy by the silver bromide.
- (2) For each absorbed  $h\nu$  a silver atom is liberated.
- (3) The mass of the latent image is determined by the number of absorbed quanta.

These conclusions can be applied at once to explain the results we have obtained above, if we remember that we are detecting the amount of light action, not by measuring directly the mass of silver produced, *but by means of a developer*. Now it is practically certain that the formation of the developable latent image is a *surface* phenomenon, and that any change brought about by the light in the interior of the grain produces no developable effect. Pearing this in mind, we may slightly modify Eggert and Noddack's conclusions, thus :—

- (a) The primary elementary process (in the formation of the *developable* latent image) consists in the absorption of a quantum of energy by the surface layer or layers of the silver-bromide crystal.
- (b) The number of silver atoms liberated is proportional to the number of  $h\nu$  absorbed by the surface layers.
- (c) The number of *developable* centres formed is proportional to the number of silver atoms liberated in the surface layers, *i. e.* to the number of  $h\nu$  absorbed by the surface layers.

If these are true, then the values obtained for  $n_2/n_1$  and  $n_3/n_2$ , when constant, are explained, and there remains the problem of the rapid increase of these ratios with decreasing exposure when the latter is small. A very simple explanation of this follows at once if we accept the idea, originally due to Svedberg (Phot. Journ. lxi. p. 332, 1921), of a minimum area of light-affected silver halide capable of acting as a developable centre. We can then picture the process to be somewhat as follows:—As soon as the light strikes the grains, silver atoms are liberated at isolated points on the grains' surface, the number of atoms formed being proportioned to the time and intensity. Only after a certain interval are there sufficient silver atoms formed within a certain minimum area on which the developer can act. Now, as we have said, the role of the developer is really that of a "detector" of the amount of light action; and since there may be an appreciable light effect without a developable centre being formed, the developer gives a *false record* of the extent of the light action at low exposures, when assumption (c) is not true. In other words, the "induction" effect, in the photographic process, is purely a development phenomenon, there being no induction with the true light action, just as there is none in the case of photoelectric substances. The ratios  $n_2/n_1$  and  $n_3/n_2$  begin to increase as soon as the exposure falls low enough for the number of centres formed by the less absorbed light to be within the induction period. In fact, an exposure can be given so that the less absorbed light gives no *developable* effect corresponding to a slight developable effect produced by equal intensity of the light more strongly absorbed, and the ratios  $n_2/n_1$  and  $n_3/n_2$  then become infinite.

The idea that the "induction" period is only a development effect is strikingly supported by Eggert and Noddack's results, that, at low exposures, the *total number of silver atoms* produced is directly proportional to the incident intensity.

It must be borne in mind that the conclusions at which we have arrived are not incompatible with the now well-established facts of the great part played by absorption phenomena in controlling the sensitivity of emulsions. For instance, we know that slight "contamination" has an enormous effect on the photoelectric activity of a metallic surface; and Langmuir's work on the catalytic poisoning of thermionic emission by absorbed gases leads us to believe that the light sensitivity of the emulsion is naturally vitally connected with the adsorption processes which have taken place on the grain surface. Thus there is nothing in the conclusions we have

drawn to contradict the statement made by one of us in a previous paper (Trans. Far. Soc. xix. pp. 290-295, 1923) that "the extreme light sensitiveness of the grain is due primarily to the presence of some substance which is not silver bromide."

The results given in this paper have been obtained with *extremely* slow emulsions. Evidence exists that with emulsions of any appreciable speed the values of  $n_2/n_1$  etc. are always much less than the theoretical values given in this paper, and decrease as the speed increases. It is possible that the explanation of this is the occurrence of "reversal" within the normal portion of the characteristic curve, as suggested recently by Svedberg (Phot. Journ. lxiv. pp. 272-274, 1924), and we hope to investigate this question. Further, by using emulsions with larger grains, the ordinary laws of reflexion and absorption will be applicable with less uncertainty.

In conclusion, we wish to express our thanks to Mr. Bloch, of the Ilford Research Laboratories, for much care and trouble in the preparation of suitable emulsions; to the National Physical Laboratory for information regarding the thermopile calibration; and to the Director of Research of the British Photographic Research Association for his interest and advice.

### *Summary.*

1. By applying the laws of reflexion and absorption to the case of a "single layer" photographic plate, the relative quantities of light energy, of different frequencies, absorbed by the grains when equal intensities of each are incident, are calculated; hence the relative number of quanta absorbed is determined.

2. It is shown experimentally that, except at low exposures, the relative number of developable centres produced by different frequencies is equal to the relative number of quanta absorbed.

3. It is suggested that the departure from this equality at low exposures is due to the fact that development does not then give a true record of the extent of the light action.

4. The results are in good agreement with the recent work of Eggert and Noddack on the proof of the Law of Photochemical Equivalence in the case of the photographic dry plate.



XCII. *On the Measurement of the Natural Frequency of an Inductance Coil at Audio-Frequency.* By H. NUKIYAMA, Professor, Tohoku Imperial University, Japan, and K. KOBAYASHI\*.

*Abstract.*

WE measure the frequency of the alternating current by the known mutual inductance and capacity with Campbell's frequency bridge. The same circuit can be utilized to determine the natural frequency of a coil used as the primary of the mutual inductance, if we know the frequency of the current and the capacity which gives the balance. In the experiment described in this paper the frequency is determined by standard tuning-forks. A theory by which the natural frequency and the self-capacity of the primary coil can be obtained by taking balance at two known frequencies is worked out. The actual method of experiment and the experimental check of this theory are also described. When the sharpness of the balance is greatly affected by the presence of the self-capacity, it can be improved by a simple modification of the circuit as shown in fig. 6.

(1) *Campbell's frequency bridge.*

When an alternating current of the angular velocity  $\omega = 2\pi f$  is transmitted to Campbell's frequency bridge, as shown in fig. 1, the condition in which the receiver current disappears is (Bibliography 1, 2, 3, 4)

$$\omega = \frac{1}{\sqrt{MC}} \quad \dots \dots \dots (1)$$

If the primary coil  $L$  of the mutual inductance  $M$  is shunted by capacity  $C_0$ , as shown in fig. 2, the above conditions must be

$$\omega = \frac{1}{\sqrt{MC + LC_0}}, \quad \dots \dots \dots (2)$$

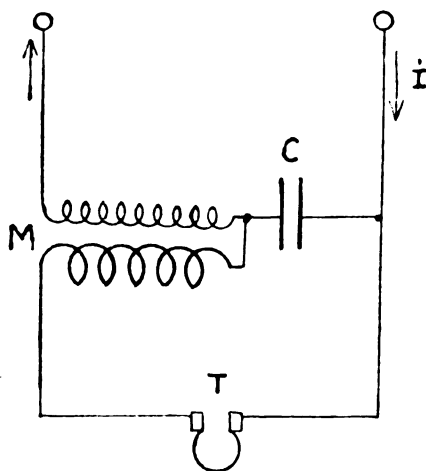
$$\omega C_0 R = 0, \quad \dots \dots \dots (3)$$

where  $L$  is the self-inductance of the primary coil and  $R$  its resistance.

Although condition (2) can be satisfied by adjusting  $M$  or  $C$ , condition (3) can not be satisfied strictly, and

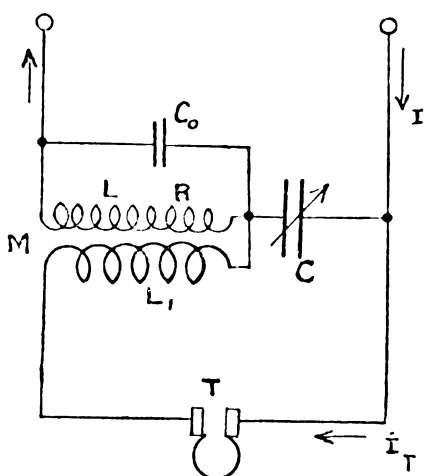
\* Communicated by the Authors.

Fig. 1.



Campbell's frequency bridge.

Fig. 2.



Campbell's frequency bridge with a shunt condenser at the primary.

the balance is not perfect. But in the case of the minimum sound, condition (2) must be satisfied, so that expressing this in the form of eq. (1),

$$\omega = \frac{1}{\sqrt{MC + LC_0}} = \frac{1}{\sqrt{M'C}} \dots \dots \dots (4)$$

$M'$  may be called the "apparent mutual inductance," and

$$M' = M + \frac{C_0 L}{C} \dots \dots \dots (5)$$

That is,  $M$  may be considered to be corrected by  $\frac{LC_0}{C}$  on account of its self-capacity  $C_0$ .

## (2) Self-capacity of a coil.

Considering that the capacity distributed along the conductors of the coil is externally equivalent to the concentrated capacity shunted across the terminals of the coil, we call the latter the "self-capacity" of the coil. By the theory above described, Campbell's frequency bridge can be utilized to determine the self-capacity of the coil.

If the self-capacity of a coil is to be determined, we construct a mutual inductance, using that coil as its primary, and a coil as its secondary of which the self-capacity correction is very slight compared with that in the primary. Campbell's frequency bridge is made of the mutual inductance and a standard condenser; the latter has either a known correction due to frequency, or a negligible percentage of it when compared with the correction of coil  $L$  due to its self-capacity. Then, determining the frequency of the current by tuning-forks, we have by (4) at its balance

$$M' = \frac{1}{C\omega^2} \dots \dots \dots (6)$$

Thus the apparent mutual inductance can be determined. If the apparent mutual inductances  $M_1'$  and  $M_2'$  at two known frequencies, and the capacities  $C_1$ ,  $C_2$  which give the balance, are measured, we have by eq. (5)

$$M_1' = M + \frac{LC_0}{C_1},$$

$$M_2' = M + \frac{LC_0}{C_2},$$

and from these equations we have

$$LC_0 = \frac{M_1' - M_2'}{\frac{1}{C_1} - \frac{1}{C_2}}, \quad \dots \quad (7)$$

$$M = M_1' - \frac{LC_0}{C_1}, \quad \dots \quad (8)$$

and, finally, the natural frequency of the coil

$$f_0 = \frac{1}{2\pi \sqrt{LC_0}} \quad \dots \quad (9)$$

The self-capacity  $C_0$  may be obtained by a similar experiment to that mentioned above, by shunting the coil by a known capacity  $C_{01}$ . In this case, by eq. (5), apparent mutual inductances  $M_1''$ ,  $M_2''$  and the capacities  $C_3$ ,  $C_4$  at two known frequencies must satisfy the following condition :

$$M_1'' = M + \frac{(C_0 + C_{01})L}{C_3},$$

$$M_2'' = M + \frac{(C_0 + C_{01})L}{C_4}$$

From these equations

$$(C_0 + C_{01})L = \frac{M_1'' - M_2''}{\frac{1}{C_3} - \frac{1}{C_4}} \quad \dots \quad (10)$$

Eliminating  $L$  from both (7) and (10), we have

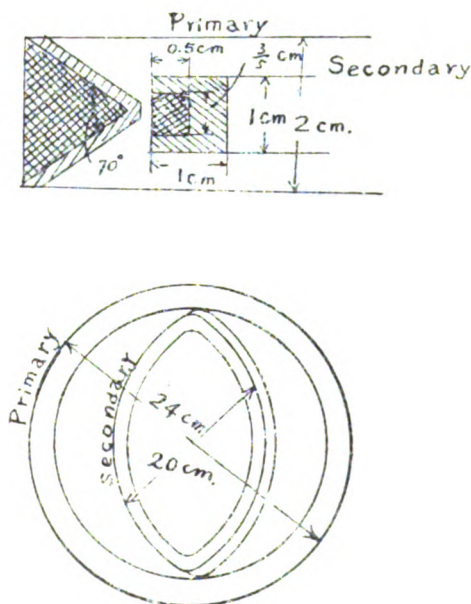
$$C_0 = \frac{C_{01}}{(M_1'' - M_2'') \left( \frac{1}{C_1} - \frac{1}{C_2} \right) - 1} \cdot \frac{(M_1' - M_2') \left( \frac{1}{C_3} - \frac{1}{C_4} \right)}{\dots} \quad \dots \quad (11)$$

### (3) Experiments.

We measured the  $LC_0$  of the primary coil of the mutual inductance as shown in fig. 3. Experiments were worked out on several coils of a different number of turns, of which we shall describe one case as an example. An alternating current was supplied to circuit B, containing Campbell's

frequency bridge, from a triode valve oscillator, as shown in fig. 4. For condenser C, Siemens' standard mica condenser and calibrated dial type air-condenser were used, the latter for fine adjustment. The frequency of the alternating current was determined by tuning the sound of the telephone receiver with Max Kohl's standard tuning-forks, adjusting the condenser C' of the triode valve oscillator.

Fig. 3.



Mutual Inductance.

The secondary of the mutual inductance may be rotated round the common axis of the primary, and the position angle of the secondary coil was measured from the position at which both coils were in the same plane. In Table I. the column marked "degree" denotes this angle, C the capacity which gives the balance, and M' the apparent mutual inductance calculated by eq. (4) using C and the angular velocity determined by tuning-forks.  $LC_0$  and M calculated by (7) and (8), using the values of M' and C at

TABLE I.—Apparent Mutual Inductance.

Degree.	$f=320.$		$f=312.$		$f=704.$		$f=960.$		$f=2048.$	
	C $\mu$ . f.	M' henry.	C $\mu$ . f.	M' henry.	C $\mu$ . f.	M' henry.	C $\mu$ . f.	M' henry.	C $\mu$ . f.	M' henry.
10 .....	0.237	1046.3	0.09154	1059.7	0.04827	1058.3	0.0256	1082	0.00472	1282
20 .....	0.29	856.1	0.10085	961.8	0.05858	874.0	0.0311	891.1	0.00586	1032.6
30 .....	0.355	698.5	0.13892	698.2	0.0729	702.4	0.0387	715.4	0.00720	844.2
40 .....	0.445	557.2	0.17468	555.2	0.0915	559.3	0.0488	567.0	0.00919	658.4
50 .....	0.574	432.0	0.22500	435.9	0.118	433.5	0.0623	444.3	0.0116	521.6
60 .....	0.770	322.1	0.3007	322.5	0.1585	323.0	0.0842	328.0	0.0158	383.0
70 .....	1.135	218.5	0.443	218.9	0.231	221.8	0.1230	225.2	0.0236	256.4
80 .....	2.000	124.0	0.783	123.9	0.413	123.9	0.1284	126.7	0.0413	140.4

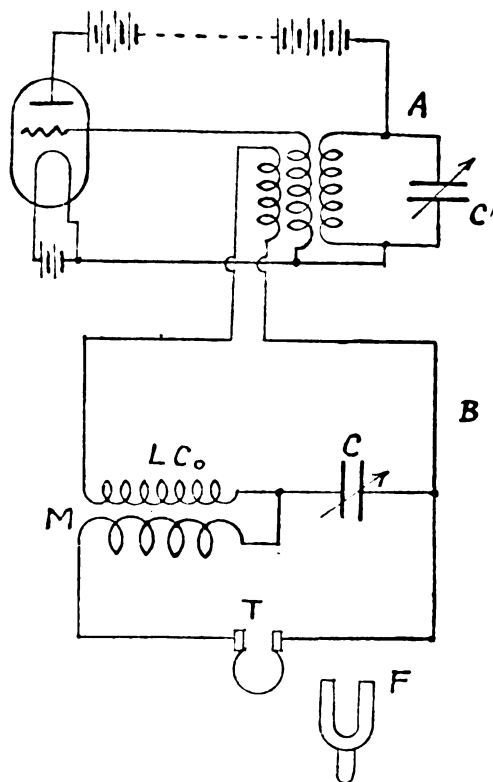
TABLE II.—( $C_0$ L and M.

Degree.	$\omega=2\pi\times320.$ $M_1$ henry.	$\omega=2\pi\times2048.$ $M_2$ henry.	$C_1$ $\mu$ . f.	$C_2$ $\mu$ . f.	M henry.	$C_0$ L sec <sup>2</sup> .
10 .....	1.0463	1.2820	0.237	0.00472	1.052	$11.35\times10^{-10}$
20 .....	0.8551	1.0326	0.290	0.00586	0.855	$10.70\times10^{-10}$
30 .....	0.6985	0.8442	0.355	0.00720	0.697	$10.65\times10^{-10}$
40 .....	0.5573	0.6584	0.445	0.00919	0.550	$9.53\times10^{-10}$
50 .....	0.4320	0.5216	0.574	0.01160	0.4307	$10.6\times10^{-10}$
60 .....	0.3221	0.3830	0.770	0.01580	0.3188	$9.13\times10^{-10}$
70 .....	0.2185	0.2564	1.135	0.02360	0.2106	$9.13\times10^{-10}$
80 .....	0.1210	0.1464	2.000	0.04133	0.1200	$9.45\times10^{-10}$
Mean .....						$10.46\times10^{-10}$

Mean ..... 10.46  $\times 10^{-10}$

$f=320$  and  $f=2048$  of Table I., are shown in Table II. The apparent mutual inductances, calculated by (5) using  $M$  and the mean value of  $LC_0=10.46 \times 10^{-10}$  sec.<sup>2</sup>, both obtained in Table II., are compared with its actually measured values in fig. 5. Coincidence of both values shows that the

Fig. 4.



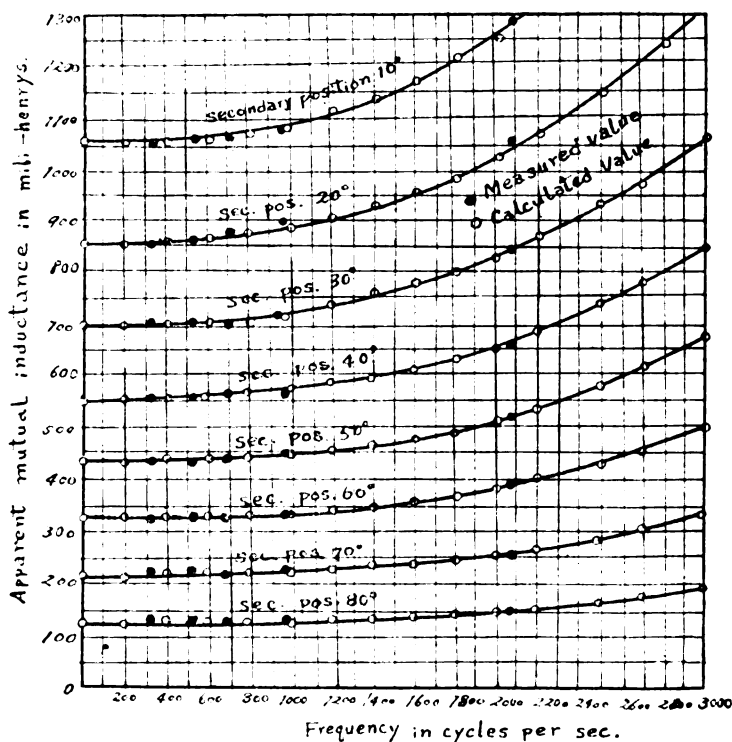
Circuit arrangement.

above-mentioned distributed capacity can be replaced by a concentrated capacity across the terminals in the range of our frequencies. As shown in Table II., the decrease of  $LC_0$  with decreasing  $M$  may be the effect of the self-capacity of the secondary coil.

(4) Method for perfect balance.

Of the conditions of the balance, eq. (2) and eq. (3), the latter cannot be satisfied in the connexion as shown in fig. 2. When the sharpness of the balance is greatly affected by the resistance of the primary, it can be improved by a simple

Fig. 5.



Change of the apparent mutual inductance by the frequency.

modification of the connexion, in which the condenser  $C$  is divided into two parts  $C_1$  and  $C_2$ , and a non-inductive resistance  $r$  is inserted in series with  $C_2$ , as shown in fig. 6. (This method was tried by our collaborator, Mr. M. Matsudaira.)

In this circuit, the conditions in which the receiver current

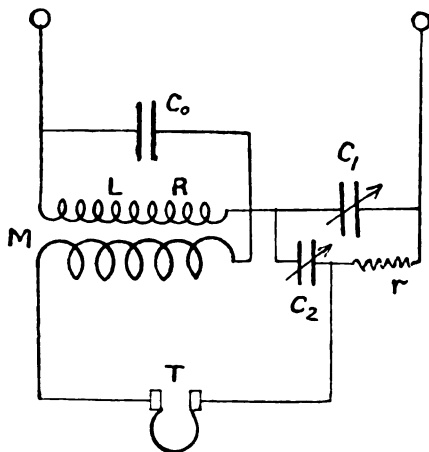


becomes zero are, putting  $C = C_1 + C_2$ ,

$$\omega = \frac{1}{\sqrt{MC + LC_0}}, \quad \dots \dots \dots (12)$$

$$C_0 R = \frac{C_1 C_2 M r}{MC + LC_0} \quad \dots \dots \dots (13)$$

Fig. 6.



Modification of the Campbell's frequency bridge to obtain a perfect balance.

Then, both equations can be satisfied at the same time by adjusting  $C_1$ ,  $C_2$ , and  $r$ , and the balance will be perfect. Yet in this case the method for determining  $M$  and  $LC_0$  stands unchanged, as the equation (12) remains the same as eq. (2). Using  $M$  and  $LC_0$  obtained by (12),  $C_0 R$  can be calculated by (13); accordingly the effective resistance of coil  $R$  can be determined if we know  $C_0$ .

### (5) *Conclusion.*

In an ordinary laboratory the greatest difficulty in this method for determining the self-capacity of the coil may be that a standard set of tuning-forks is needed. But if we were trained to calibrate the frequency of the alternating current as a multiple of the frequency of a tuning-fork, only one tuning-fork would be needed. It is a merit of this method that the sources of error due to the change of apparent constants of the circuit element are greatly eliminated by the simplicity of the circuit.

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XCIH. *The Thermal Conductivity of Bismuth in a Transverse Magnetic Field.* By F. A. WARD, B.Sc.(Lond.), A.Inst.P.\*

INVESTIGATIONS of the thermal conductivity of bismuth in a magnetic field when the lines of force are perpendicular to the direction of heat-flow have been made by various observers. Leduc† found a decrease of 5·7 per cent. in a field of 7800 c.g.s. units. Nernst‡ in 1887 could detect no change. Ettingshausen§ found a diminution from 2 to 5 per cent. in a field of 9000 c.g.s. units. Van Everdingen|| 5·8 per cent. in a field of 6000, and Blyth¶ a diminution of 0·05 per cent. in a field of 3500 c.g.s. units. Livens\*\*, assuming the free electron theory, has developed a formula according to which the thermal conductivity of solids should increase in the magnetic field. This is contrary to the experimental results.

The material used in the present investigation was pure bismuth supplied by Messrs. Johnson & Matthey. Some of the metal was powdered and placed in a glass tube about 4 mm. in diameter from which the air was withdrawn. While evacuated, the tube was heated until the whole of the metal was melted. It was then allowed to cool slowly, and on solidification the glass tube was broken, a fairly uniform cast rod being obtained in this way. From a number of rods prepared in this manner two were selected for the investigation.

\* Communicated by Dr. L. Lownds.

† *C. R.* cii. p. 358 (1886).

‡ *Wied. Ann.* xxi. p. 760 (1887).

§ *Wied. Ann.* xxxiii. p. 129 (1888).

|| *Journ. de Phys.* (3) x. p. 217 (1901).

¶ *Phil. Mag.* (6) v. p. 529 (1903).

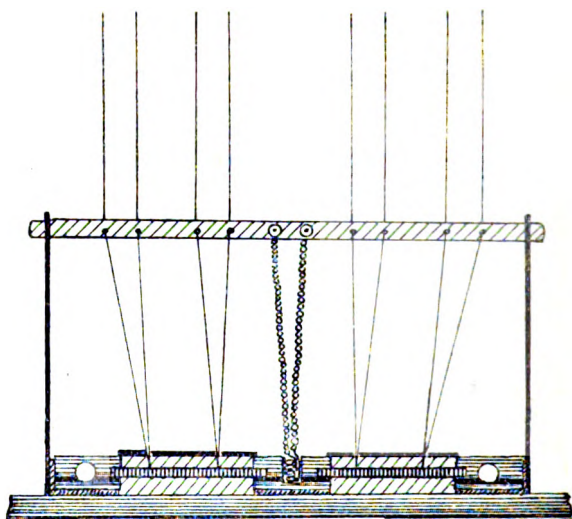
\*\* *Phil. Mag.* (6) xxx. p. 526 (1915).

The dimensions of the selected rods were: (1) length 7.6 cm., diameter 0.35 cm.; (2) length 7.6 cm., diameter 0.40 cm.

The specific electrical resistance of these rods was  $119 \times 10^{-6}$  ohm-cm. and  $119.2 \times 10^{-6}$  ohm-cm. respectively.

The rods were fixed between copper blocks A, B, C (fig. 1).

Fig. 1.



ELEVATION



PLAN

SCALE  $\frac{1}{2}$ 

Heat was supplied at a constant rate to the central block A by means of a small coil carrying a current and embedded in the centre of this block. Water circulated through the outer coppers B and C. The whole was well lagged, and when steady conditions obtained, the temperature gradient on each bar was determined by the copper-constantan-thermocouples (1, 2, 3, 4). The apparatus was mounted so that either of the bars could be placed in an intense uniform magnetic field.

If  $W$  denote the rate of supply of heat to the heating coil,  $K$  and  $K_1$  the thermal conductivities of bismuth without and with the field ;

$A_1$  and  $A_2$  the sectional areas of the rods containing junctions (1) and (2), and (3) and (4) respectively ;

$g_1$  the temperature gradient between the thermo-junctions between the pole-pieces,  $\left\{ \begin{array}{l} \text{when there is} \\ \text{no magnetic} \end{array} \right.$   
 $g_2$  the temperature gradient between the thermo-junctions outside the pole-pieces,  $\left. \begin{array}{l} \text{field ;} \end{array} \right\}$

$G_1, G_2$  the corresponding gradients when the magnetic field is impressed ;

$X$  the heat-losses due to radiation etc., which may be assumed the same in both cases.

Then

$$W = KA_1g_1 + KA_2g_2 + X,$$

$$W = K_1A_1G_1 + KA_2G_2 + X,$$

whence

$$\frac{K_1}{K} = \frac{A_1g_1 + A_2g_2 - A_2G_2}{A_1G_1}.$$

The heating-coil was of nichrome wire (gauge 40), wound on slate and insulated from the copper block. It was firmly cemented in the cavity, and the leads from it, insulated by glass beads, passed through holes in the fibre cross-piece forming the top of the framework which carried the rods and copper blocks. The heating current was supplied by a battery of accumulators, this circuit containing regulating resistance and milliammeter. The bismuth rods fitted into holes in the copper blocks, and were secured in position by means of set screws. The thermocouples were of copper constantan (gauge 36). Small holes were drilled in the rods to receive the junctions, and they were soldered in position with a little powdered bismuth to secure good thermal contact.

The distance between junctions (1) and (2) was 1.89 cm., and between (3) and (4) 1.98 cm. The rods were lagged with lightly-packed cotton-wool, which was kept in position by rectangular fibre strips screwed to the copper blocks.

The thermocouple wires passed through slits cut in the upper fibre strips and thence through holes in the fibre cross-piece. The whole was screwed to a brass bar of rectangular section, from which it was insulated. The bar was supported by guides in an outer copper shield, and could move through



*2nd Series. Junctions 3 and 4 between the pole-pieces.*

Expt. Nos.	11.	12.	13.	14.
$t_1$ .....	261.8	261.2	204.5	204.4
$t_2$ .....	257.0	257.8	202.8	203.4
$T_1$ .....	264.3	264.3	208.2	208.2
$T_2$ .....	260.2	260.2	206.2	206.2

*3rd Series. Junctions 1 and 2 between the pole-pieces.  
Field reversed.*

Expt. Nos.	15.	16.
$t_1$ .....	272.0	289.6
$t_2$ .....	211.7	224.5
$T_1$ .....	277.7	295.2
$T_2$ .....	215.5	226.8

These numbers were converted into values for  $g_1, g_2, G_1, G_2$  by dividing by the distance between the junctions concerned, and the average value of  $K_1/K$  deduced by combining the observations as follows :—

Expt. Nos. 1 to 6 .....	96.23	} { .....96.52 } .....96.95 } .....96.78
2 to 7 .....	96.20	
3 to 8 .....	96.55	
4 to 9 .....	97.05	
5 to 10 .....	97.01	
Expt. Nos. 11, 12, 13, 14 .....	.....	96.80
Expt. No. 15, 16 .....	.....	96.70
Mean..... $K_1/K = 96.73$		

The average diminution of the thermal conductivity of bismuth is 3.22 per cent. in a transverse magnetic field of 5370 c.g.s. units. With a field of 6260 c.g.s. units the heating of the electromagnet became excessive, so that prolonged observations could not be carried through. The decrease in this case was of the order 5 per cent.

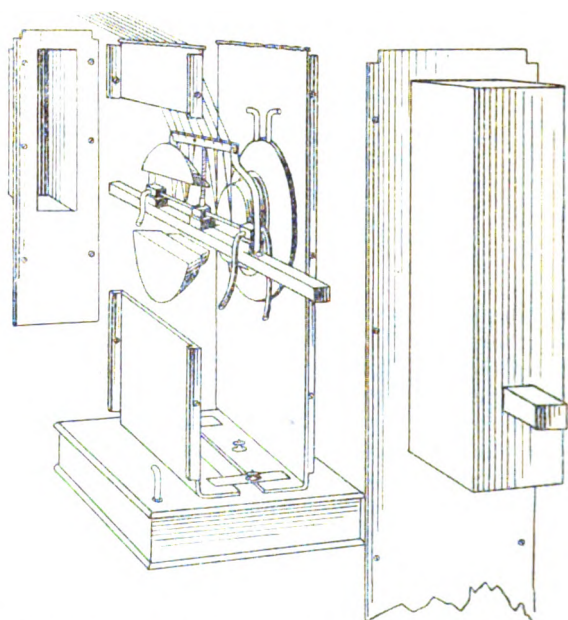
My thanks are due to Dr. Lownds for suggesting this work to me and for his advice and help during its progress.

Physics Department,  
Chelsea Polytechnic,  
June 1924.

these so as to place either bismuth rod between the poles (fig. 2).

To ensure steady conditions, it was found necessary to protect the apparatus from the heating effects of the current circulating in the electromagnet coils. This was done by building round the apparatus a shield of stout sheet copper. This was made in sections (see fig. 2), which could be firmly bolted to one another. The water after circulating through the end coppers was led to the base of the shield, which was a hollow metal box, and thence through copper formers

Fig. 2.



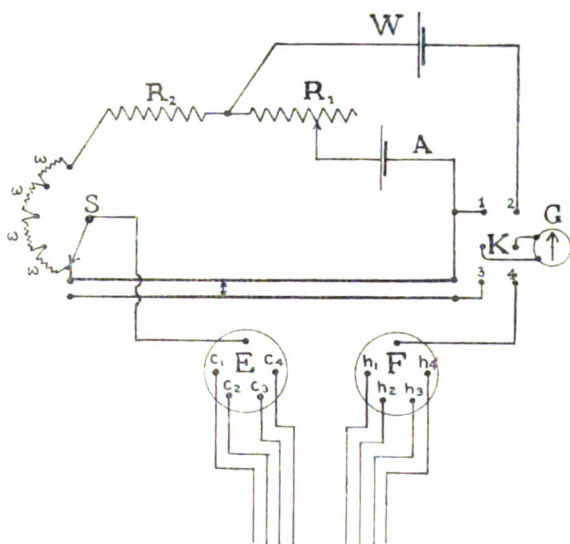
fitting the pole-pieces and in good contact with the vertical sides of the shield. This water, before entering the copper blocks, passed through a metal worm 60 ft. long, contained in a large tank of water to secure uniformity of temperature.

Fig. 3 shows diagrammatically the arrangement for measuring the E.M.F.'s. of the thermocouples.  $W$  is a standard cadmium cell,  $R_2$  a resistance of 1013 ohms in series with four accurately adjusted ohm coils and a manganin wire (1 m. long), also adjusted to 1 ohm by a resistance in parallel with it.  $A$  is an accumulator. By connecting (1) and (2) to the galvanometer terminals and adjusting  $R_1$ ,



the potential drop along the manganin wire when no current flows through the galvanometer is made 1 microvolt per mm. E and F are mercury cups connecting to the hot and cold junctions of the several thermocouples. To balance the E.M.F. of a couple, connexions  $c_1h_1$  to E and F are made, (3) and (4) are connected to the galvanometer, and (1) and (2) are broken. The slider on the manganin wire is then adjusted till there is no deflexion in the galvanometer. To avoid disturbing thermal effects at the contact maker a second manganin wire ran alongside the bridge wire, and the contact maker bridging the two wires was of manganin. The apparatus was sensitive to less than 0.5 microvolt.

Fig. 3.



The electromagnet was of the split toroid type, with conical pole-pieces shaped to give a uniform field. The diameter of the pole-pieces was 5 cm., and they were adjusted by means of a distance-piece to a gap width of 2 cm. This was the minimum distance which would accommodate the apparatus. The field strengths were measured ballistically by means of a search coil and standardizing solenoid. The magnetizing field used in the experiments was 5370 c.g.s. units.

The method of a typical experiment was as follows:—The water circuit, heating current, and electromagnet current



were started at about 10 A.M. The magnetizing current at first circulated in opposite directions through the two limbs of the magnet, so that the field was not excited. The ammeters were observed at intervals, and kept at constant values by regulating resistances. Observations were usually commenced after an interval of about 6 hours, after which time conditions were usually steady. Readings of the thermocouples were taken with no field, and then the field was impressed. After about  $1\frac{1}{2}$  hours the thermocouple temperatures were again steady and were recorded. The current was again reversed in one of the limbs, and a third set of thermocouple observations taken after a further period of  $1\frac{1}{2}$  hours.

Table I. shows a typical set of observations.  $t_1$  is the difference between balance points in mm. on the potentiometer wire for the junctions between the pole-pieces;  $t_2$  the difference for those outside, when there is no field;  $T_1$ ,  $T_2$  the corresponding data when the field is excited.

TABLE I.

Time .....	4.54.	5.06.	5.15.	5.24.	5.41.	5.52.	6.00.
$t_1$ .....	212	213	211	210	213	213	213
$t_2$ .....	211	211	211	211	211	211	211
Time .....	—	—	6.41.	7.04.	7.16.	7.27.	7.26.
$T_1$ .....	—	—	216	216	215	215	214
$T_2$ .....	—	—	216	216	216	215	215
Time .....	—	—	—	8.36.	8.41.	8.53.	9.14.
$t_1$ .....	—	—	—	214	214	213	213
$t_2$ .....	—	—	—	213	211	210	211

In all, sixteen experiments were performed, giving the following average values :—

*1st Series. Junctions 1 and 2 between the pole-pieces.*

Expt. Nos.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
$t_1$ .....	307.6	219.8	218.8	206.2	205.4	212.6	213.5	298.2	278.2	277.8
$t_2$ .....	314.8	218.2	219.8	206.3	204.2	211.0	211.2	299.0	280.8	279.8
$T_1$ .....	313.2	222.9	222.9	209	205.0	215.2	215.2	301.0	280.4	280.4
$T_2$ .....	317.8	224.5	224.5	210.8	207.6	215.6	215.6	304.1	284.0	284.0

*2nd Series. Junctions 3 and 4 between the pole-pieces.*

Expt. Nos.	11.	12.	13.	14.
$t_1$ .....	261.8	261.2	261.5	264.4
$t_2$ .....	257.0	257.8	262.8	263.4
$T_1$ .....	264.3	264.3	268.2	268.2
$T_2$ .....	260.2	260.2	266.2	266.2

*3rd Series. Junctions 1 and 2 between the pole-pieces.  
Field reversed.*

Expt. Nos.	15.	16.
$t_1$ .....	272.0	289.6
$t_2$ .....	211.7	224.5
$T_1$ .....	277.7	295.2
$T_2$ .....	215.5	226.8

These numbers were converted into values for  $g_1, g_2, G_1, G_2$  by dividing by the distance between the junctions concerned, and the average value of  $K_1/K$  deduced by combining the observations as follows :—

Expt. Nos. 1 to 6 .....	96.28	} {	.....96.52 } .....96.95 }	} .....96.78
2 to 7 .....	96.20			
3 to 8 .....	96.55			
4 to 9 .....	97.05			
5 to 10 .....	97.01			
Expt. Nos. 11, 12, 13, 14 .....	.....		.....	96.80
Expt. No. 15, 16 .....	.....		.....	96.70
Mean..... $K_1/K = 96.78$				

The average diminution of the thermal conductivity of bismuth is 3.22 per cent. in a transverse magnetic field of 5370 c.g.s. units. With a field of 6260 c.g.s. units the heating of the electromagnet became excessive, so that prolonged observations could not be carried through. The decrease in this case was of the order 5 per cent.

My thanks are due to Dr. Lownds for suggesting this work to me and for his advice and help during its progress.

Physics Department,  
Chelsea Polytechnic,  
June 1924.

X(CIV). *Low-Voltage Glows in Hydrogen.* By G. STEAD, M.A., Reader in Physics in the University of London, and B. TREVELYAN, B.A., Yarrow Research Student, Girton College, Cambridge\*.

#### INTRODUCTION.

THE type of discharge-tube employed in the present investigation, and described in a previous paper †, shows peculiarities not found in the more usual forms of two- and three-electrode thermionic tubes. The essential features are (1) the use of a very open grid close to the filament, (2) the absence of an anode, and (3) the large volume on the side of the grid remote from the filament. Under these conditions a large emission can take place from the filament when the difference of potential between the grid and the filament is quite low, and a considerable proportion of the emitted electrons passes through the grid into the space beyond, giving rise to intense ionization in a large volume of gas. Some of the positive ions so formed are drawn into the region between the grid and filament, some are repelled by the grid to the walls of the tube, which may thus become charged to a considerable potential, whilst others must recombine before reaching either the filament or the walls. It is only those positives which reach the neighbourhood of the filament before recombining that are effective in reducing the negative space-charge and causing an increase in the filament-grid current.

The present investigation is concerned chiefly with hydrogen. The results obtained seem to indicate (1) some kind of action between hydrogen and a glowing tungsten filament; (2) the formation in the discharge-tube of a substance which shows no evidence of ionization below 40–50 volts, whereas ordinary hydrogen in the same tube ionizes at 20–27 volts; (3) the formation of some compound, [possibly identical with (1)], which is condensable in liquid air, but unstable at ordinary temperatures.

The large-volume ionization in the region beyond the grid renders this type of tube particularly suitable for studying chemical actions. It also seems likely that this form of tube would favour the formation of negative ions, and these would probably show considerable chemical activity. It is known (from J. J. Thomson's experiments on positive rays) that hydrogen is capable of forming  $H_2$  and  $H$ .

\* Communicated by the Authors.

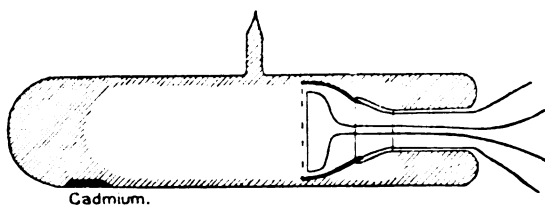
† Stead & Stoner, Proc. Camb. Phil. Soc. xxi. p. 66 (1922).

Electro-positive elements, such as mercury, nickel, and tungsten, would perhaps be more likely to combine with negative hydrogen ions than with positive ions, and also a molecule such as  $H_2$  might be produced by a combination of  $\bar{H}_2$  with  $\bar{H}$ .

The following investigations were a continuation of the work of Stead and Stoner\* on low-voltage glows obtained in mercury vapour by means of a thermionic tube of special design.

**CADMIUM.**—Preliminary experiments were performed with cadmium vapour in a tube of the same form as that used for mercury (fig. 1). The grid was an open one of zigzag

Fig. 1.



pattern, with about three turns, and of length just less than the diameter of the tube; there was no anode, the grid being connected to the positive end of the high-tension battery. The tungsten filament (about 0.089 cm. diameter) was about 1.5 mm. from the grid. A small stick of pure cadmium was placed in the tube, which was evacuated and baked in the usual way; the pressure on sealing off, as measured by the McLeod gauge, was less than 0.001 mm. of mercury. Different pressures of cadmium vapour could be maintained in the tube by keeping it as nearly as possible at different constant temperatures by means of an electric furnace.

#### OBSERVATIONS.

The same type of characteristic curve was obtained as in the case of mercury vapour (fig. 2). The following points were observed:—

(1) The sudden jump to saturation again occurred, synchronous with the appearance of the glow, and the corresponding fall of current from the saturation value occurred at a lower voltage than the rise.

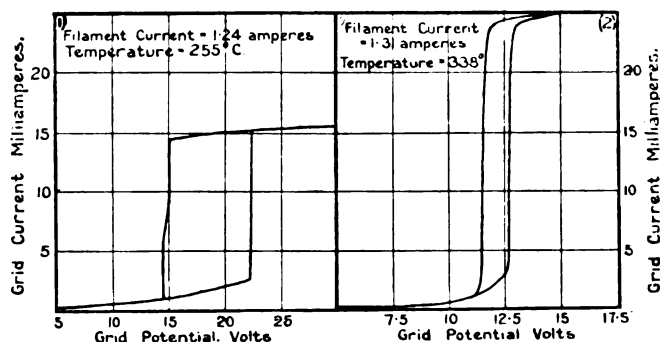
\* *Loc. cit.*

(2) The striking potential again decreased with increasing pressure till an optimum pressure was reached, at which the striking potential was a minimum (it increased with further increase of pressure).

(3) At the point of minimum striking potential, the area of the hysteresis loop was a maximum, and with sufficiently high pressure the hysteresis loop disappeared entirely and the currents were very small.

(4) The glow, as before, could be made to move up and down the tube by increasing or decreasing the voltage within limits; the spectrum of the glow was not examined in detail, but the ordinary line spectrum of cadmium was prominent.

Fig. 2.



It seems likely that, since cadmium and mercury show similar results under similar conditions, other monatomic gases and vapours would behave in the same kind of way.

**HYDROGEN.**—The valve used in the experiments on hydrogen was identical in design with the cadmium and mercury valves, except that it had two outlet tubes, one attached to the evacuating apparatus, and the other to the source of hydrogen, which was, at first, a strong solution of phosphorus pentoxide in water. This was electrolyzed, and the hydrogen was passed over dry phosphorus pentoxide and through a trap immersed in liquid air. In later experiments a palladium tube was used as a source of hydrogen, but it was found that the change did not affect the observations. The discharge-tube was baked out as usual, and was evacuated each day before experimenting; a trap immersed in liquid air was placed between the main tube and the pump, to condense as much mercury vapour as possible.

## OBSERVATIONS.

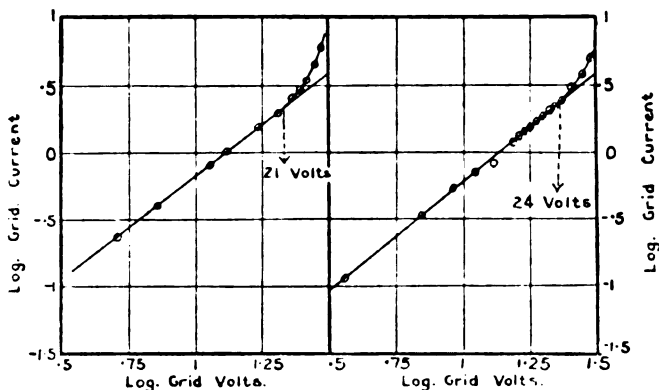
## I. OSCILLATIONS.

A small amount of hydrogen at a pressure of about 0.5 mm. was let into the main tube, and the characteristic curve, grid current/grid potential, was plotted. The type of curve obtained was quite different from that shown by the monatomic vapours. There was no sudden jump to saturation, but the curve appeared quite continuous, giving a gradual increase of current till a potential of about 30 volts was reached. At this point a small jump occurred in the current, and then a curious instability was observed. Instead of remaining at a steady value for constant voltage, the current rose slowly and regularly to a maximum, and then fell again to a minimum, then increased again, and so on with a regular oscillatory movement of definite period.

Fig. 3.

Filament current 1.16 amp.  
Pressure .057 mm.

Filament current 1.0 amp.  
Pressure .05 mm.



The rise and fall of the current corresponded to a motion of the glow up and down the tube. The small jump at the minimum voltage for this oscillatory condition (about 27–30 volts) probably coincided with the first appearance of the glow, though it was difficult to observe the latter, as it was very faint at first, the intensity increasing gradually with the extension of the glow along the tube. On plotting the logarithms of the current and potential up to the oscillating point, it was seen that a rise in the power curve occurred at about 20–25 volts; the exact point varied with the conditions (filament current, pressure, etc.) (fig. 3).

Preliminary experiments indicated that in general the time of oscillation decreased with increasing voltage. Under favourable conditions, with an optimum pressure of about  $\cdot 04$  mm., oscillations could be observed up to at least 80 volts on the grid, but to obtain oscillations at these higher potentials it was essential to perform a step-up process. The oscillatory state was first produced at a low potential, *e.g.* at about 40 volts, and the voltage then increased by steps of about 2 volts, the system being allowed to settle into the oscillatory state at each step, which it would do if left alone for a few minutes. The oscillations were followed by watching the pointer of the milliammeter, and on some occasions it was possible, by means of the step-up process, to observe an oscillation (at a grid potential of about 80 volts) which was so rapid that it was only shown by a trembling of the pointer. If a high voltage was applied to the grid at first, without the step-up process, a fairly steady current was shown with no oscillations.

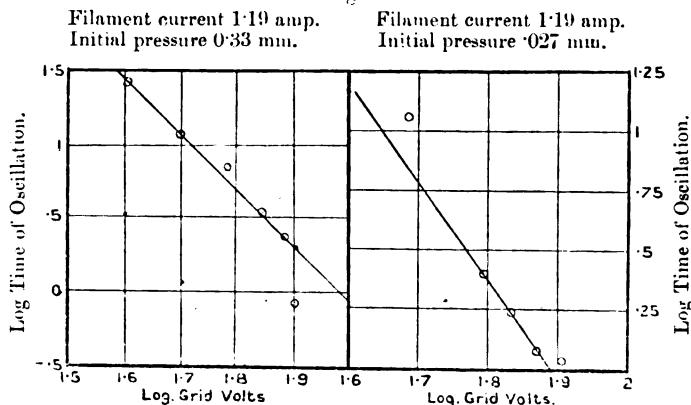
Rough observations made on the spectrum of the glow by means of a Hilger spectroscope showed that in the latter case the Balmer lines were the most prominent and the secondary spectrum faint; but when the glow grew to a maximum at low voltages, there was a corresponding gradual increase in intensity of the secondary spectrum. If the glow was thus allowed to grow to a maximum, and the high voltage then applied to the grid, without any intermediate steps, a momentarily very large current was obtained, with a brilliant secondary spectrum, but this decreased very rapidly to a minimum, and the secondary spectrum again became faint, leaving the Balmer lines prominent.

The oscillations were studied in more detail, and the following results were obtained:—

(1) *The frequency of oscillation* increased regularly with increasing voltage. If the logarithm of the time of oscillation is plotted against the logarithm of the grid voltage, the points seem to lie approximately on a straight line (fig. 4 a). The extreme values for high and low voltages are somewhat off the line, but it was impossible to keep the pressure constant during a series of observations extending over any length of time. The three lines corresponding to the three series taken gave a mean slope of 3.9. The frequency of oscillation was therefore approximately proportional to the fourth power of the grid voltage. Pressure changes during the oscillations could not be investigated, as there was a general pressure decrease all the time, which made observations on a slow oscillation unreliable, and it was

impossible to follow the rapid oscillations with the McLeod gauge, but changes of pressure accompanying similar changes of current were observed (see later) with another form of tube.

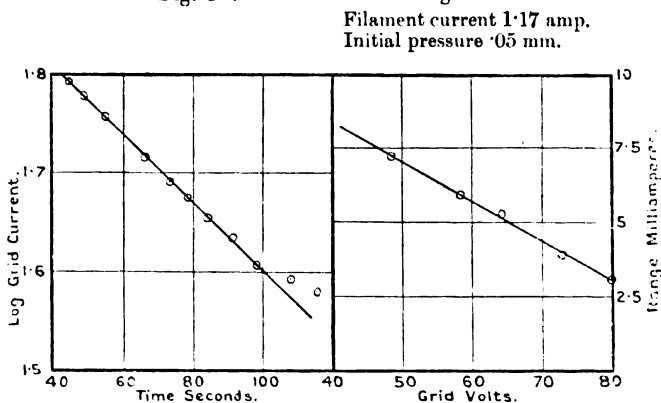
Fig. 4 a.



(2) *Variation of Current with Time.*—During the fall of one oscillation from maximum to minimum, the current decreased with the time; the curve was approximately exponential in form, but with irregularities near the maximum and minimum (fig. 4 b). The maximum currents often reached several hundred milliamperes.

Fig. 4 b.

Fig. 4 c.



(3) *The range of oscillation* varied directly with the grid voltage when the oscillation had reached a steady condition (fig. 4 c). Each time the grid potential was increased, the range of oscillation was at first rather irregular, but settled



down to a fairly constant value. This was most easily seen with slow oscillations of large amplitude, the range decreasing from the initial value, while the time of oscillation showed a slow increase, and may probably be largely accounted for by the general pressure decrease due to absorption of hydrogen into the walls. With rapid oscillations the steady condition was reached more quickly, though there was a subsequent slow increase in the time of oscillation, again probably due to change of pressure; for instance, an oscillation of approximately constant period was maintained for ten minutes, and the change of period was only appreciable after this time.

TABLE I.

Initial pressure.	Final pressure.	Fil. current.	Grid volts.
•0385 mm.	•033 mm.	1.2 amps.	80
Number of oscillations in successive intervals of 10 seconds.			
11, 10, 11, 11, 11, 12, 12, 12, 12, 12, 12, 11, 11, 11, 11, 11, 12, 12, 10, 10, 11, 10, 10, 10, 10, 10, 10, 10, 10, 10, 11, 10, 11, 10, 10, 10, 10, 11, 10, 12, 14, 13, 12, 12, 12, 11, 12, 12, 11, 10, 11, 11, 11, 8, 10, 12, 8, 9, 10, 9, 10, 9, 8, 9, 9, 10, 10, 8.			

There is not much change here for at least ten minutes.

It may therefore be assumed that the time of oscillation would be constant for constant pressure. Greater changes of pressure had a marked effect on the time of oscillation.

(4) *The form of oscillation*, when fairly rapid, was a gradual rise, then a jump to the maximum, then a gradual fall and a jump to the minimum.

(5) An attempt to obtain an oscillatory glow with a stream of hydrogen passing through the tube was unsuccessful.

In case the oscillatory phenomena were due to the periodic charging up and discharging of the walls of the tube, the experiments were performed with a tube whose walls were silvered internally and connected to the negative end of the filament, but it was still possible to obtain the oscillating glow under these conditions.

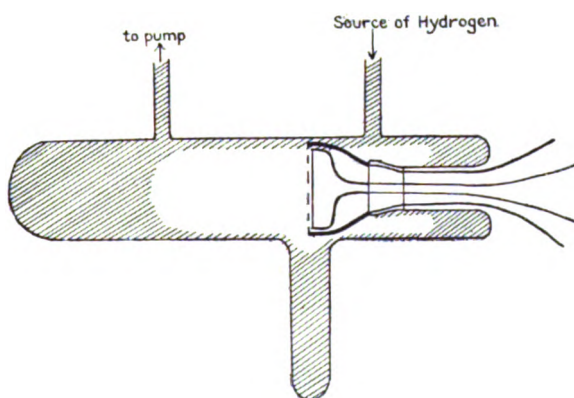
An attempt was made to exclude mercury as far as possible by baking the main tube, with liquid air round traps on either side, till the mercury lines were no longer visible in the spectrum of the glow. The oscillations could still be obtained, though not so easily as before. Of course it was impossible to remove all the mercury by this means, but the experiments seemed to indicate that mercury was not an essential factor for the production of the oscillations.

Later experiments with other tubes of as nearly as possible the same design, and used under approximately the same conditions, were unsuccessful in producing regular oscillations, though at low pressures irregular oscillations were shown. It seems likely, therefore, that in the first case an optimum spacing of the grid wires had occurred accidentally. The same electrodes were used for the silvered and unsilvered tubes, but were afterwards unfortunately broken. Further attempts will be made to reproduce the oscillations with grids of various spacings. It is also probably necessary to have carbon vapour present (from tap grease) to produce the oscillations, but this alone is not sufficient.

## II. EFFECT OF LIQUID AIR.

Another tube of slightly different design was prepared, with a collecting tube at right angles to the main tube below the filament (fig. 5). This collecting tube was immersed in

Fig. 5.



liquid air, in order to collect any condensible gases. At the same time another McLeod gauge was attached near the main tube, so that the gauge and tube could be shut off by taps from the rest of the apparatus. The main results with this tube were as follows:—

(1) *Disappearance of Hydrogen.*—Very brilliant glows were obtained; these showed intense secondary spectra, and very large currents up to 700 milliamps. The glow did not oscillate, but grew to a maximum, and gradually increased

in brightness, then fell back slowly and disappeared when close to the filament; it could not be produced again by increasing the filament current, and it was found that nearly all the hydrogen had disappeared into the collecting-tube. The process could be repeated any number of times. Sometimes the glow could be temporarily regenerated by a slight decrease in filament current, but would soon disappear again.

(2) *Appearance and Disappearance of the Glow*.—When the glow had run back, it could also be regenerated by increasing the grid potential, and by a step-up process be made to disappear at successive increasing grid potentials.

(3) *Variation of Pressure with Current*.—Oscillations could not be obtained with this tube, either with or without liquid air on the collecting-tube. The nearest approach to the oscillating condition was shown by allowing the glow to grow and the current to increase while there was a low potential on the grid, say 35 volts, and the pressure noted at the maximum; a high potential, say 80 volts, was then put on the grid, the current diminished rapidly, and it was found that the pressure rose. A typical example is shown in the following table.

TABLE III.

Pressure. (300 mark of gauge.)	Position of glow.	Grid volts.	Grid current. (milliamps.)
277	max.	30.5	grows to 55
281.5	min.	81.5	falls to 6
258.5	max.	30.5	grows to 46
274	min.	81.5	falls to 6.25
256.5	max.	32	grows to 42
263	min.	82	falls to 6.1

(4) *Return of Pressure*.—Yet another pressure effect was observed. Readings of the McLeod gauge when the filament was put on showed the usual fall of pressure, but on switching off the filament a rise in pressure took place, sometimes to nearly the initial value. This was a very definite effect, usually more marked the greater the current to the grid. Several series of readings were taken, of which one is given below. The pressure readings were taken as quickly as the McLeod gauge would allow, so that about one minute elapsed between  $P_2$  and  $P_3$ . The time between  $P_1$  and  $P_2$  varied, but was generally of the order of 10 to 60 seconds.

TABLE IV.

Grid volts.	Initial pressure. $P_1$ mm.	Pressure on switching off. $P_2$ mm.	Pressure on standing. $P_3$ mm.
(a) 29	·0545	·0475	·0505
	·0505	·046	·05
	·05	·046	·049
	·049	·046	·053
(b) 49	·055	·0495	·055
	·055	·050	·053
(c) 60	·057	·051	·059
	·059	·052	·059
(d) 90	·063	·059	·063
(e) 127	·064	·060	·064

*a, b, c, d, e*, are examples selected from a longer series; some intermediate voltages are not given, so that for a change of voltage in the table the pressure readings are not consecutive.

This return of pressure must be distinguished (as quite different) from the changes of pressure observed during the variation of the glow. For the latter effect it was essential that the filament should be on continuously; but the former effect was not apparent unless the filament was switched off, and the tube allowed to stand for at least half a minute.

(5) *The gas liberated on removing the liquid air* from the collecting-tube was investigated. The method first employed was that of sparking in a quartz capillary tube substituted for the glass capillary above the bulb of the second McLeod gauge. External tinfoil electrodes were used, and the discharge from the secondary of an induction coil passed through the gas trapped in the gauge. The observations were made on the change of pressure at constant volume. Very irregular results were obtained; the ratio of the volume after sparking to the volume before sparking varied between extremes of about seven and one. The spectrum of the discharge showed strong carbon bands in addition to the hydrogen spectrum. Control experiments with ordinary hydrogen gave a ratio less than one, though carbon lines were still present in the spectrum, probably due in this case to impurities on the surface of the gauge and mercury, but they were much less prominent. Control experiments with hydrocarbons such as methane and ethane gave an increase in volume on sparking, and bright carbon and hydrogen lines.

It seems probable that in these experiments very active hydrogen was formed in the tube, and this combined readily with carbon impurities. The most likely source of the latter was tap grease; although it has a small vapour-pressure, it could distil over into the main tube at night. Another source might be the carbonates of the glass itself. The taps were replaced by mercury barometer columns, and after running the tube for some time under these conditions, the sparking ratio decreased and was sometimes less than one. The hydrogen also did not disappear so readily; but even after prolonged use it did not seem possible to eliminate the carbon lines from the glow and spark spectrum of the liberated gas, part of which appeared to be non-recondensable.

### III. QUARTZ TUBE.

In order to eliminate the carbon impurities as far as possible, a quartz tube was constructed. It was similar to the glass tube, except that it had one outlet only, opposite the collecting-tube, and the electrodes were so arranged that the axis of the filament was in a straight line with the axis of the collecting and outlet tubes. The quartz was heated red hot every day, with liquid air surrounding a trap between it and the pump and nearest mercury cut-off, so that it might be assumed that after prolonged use there was very little carbon left; a large part of the mercury present would also be removed by heating, though a certain amount would still be left on the electrodes etc.

With liquid air round the collecting-tube, the glow did not run back as before, except at very low pressures. In the latter case a faint secondary glow was left after the bright primary one had disappeared; this secondary glow had also been seen with the glass tube. At higher pressures large currents were obtained up to about 500 milliamperes. They were accompanied by bright glows, showing a marked secondary spectrum of hydrogen. The optimum pressure for this condition was of the order of  $\cdot 07$  mm., and the optimum voltage about 38 volts; a definite time was required for the glow to grow to a maximum. Further points were observed on experimenting with this tube:—

(1) *Disappearing Glow*.—In place of the run back and disappearance of the glow, which were obtained easily with the glass tube, another type of disappearing glow was seen. Under favourable conditions of pressure, and when the current had been allowed to grow slowly to a maximum, if the potential lead was removed from the battery for a few

seconds and then replaced, the current was smaller than before, and the glow had disappeared. If the potential was then increased by a few volts, the glow and large current would appear again, and could once more be made to disappear, and the process could be repeated up to the limit of the battery. This effect is similar to that observed with the glass tube (2). It seems that this "artificial disappearance" is not a simple pressure effect, for though it is more easily produced at low pressures, it can also occur at pressures quite sufficient to show the ordinary ionization glow under ordinary conditions. Of course at low pressures the glow is very faint, and might then appear to be absent, but other evidence supports the conclusion that the gas in the tube is in an abnormal condition.

(a) The disappearance cannot occur without liquid air round the collecting-tube. Without it, a somewhat similar effect could sometimes be produced at very low pressures, but only up to about 47 volts. In this case the pressure was probably diminished by absorption into the walls, and became too low to maintain a glow at the lower voltages. With liquid air round the tube the glow would disappear easily at higher pressures and up to at least 80 volts. The experiments were not usually carried further, though it was possible at low pressures to carry it up to at least 180 volts on the grid; the upper limit of disappearance was apparently higher the lower the pressure.

(b) When the glow had disappeared, it could be regenerated by removing the liquid air from the collecting-tube, though this involved very little general pressure change.

(c) When the glow had disappeared at one voltage, and was regenerated at a higher, if the lead was put back in the first position, the glow would sometimes appear again, the next removal causing it to disappear once more, so that the first disappearance could not have been simply due to a fall of pressure.

(d) If the characteristic curve for the tube (grid current/grid voltage) was plotted when liquid air was not on the collecting-tube, the upward bend in the log curve due to ionization occurred at about 20–27 volts (the exact point depending on filament current, pressure, etc.) (fig. 6a). If, however, the characteristic was plotted for the tube in the "disappeared" condition, at the same order of pressure, the upward bend did not occur until the grid potential had a much higher value, such as 40, 50, or 60 volts, the position of the bend depending upon the potential at which the glow had been made to disappear (fig. 6b).

Fig. 6 a.  
Ordinary hydrogen.  
Quartz tube.

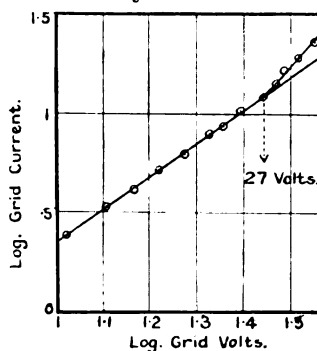


Fig. 6 c.  
Ordinary hydrogen. Quartz tube.  
(Low pressure.)

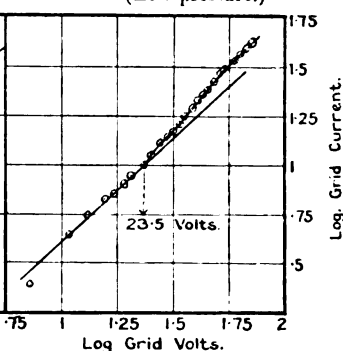
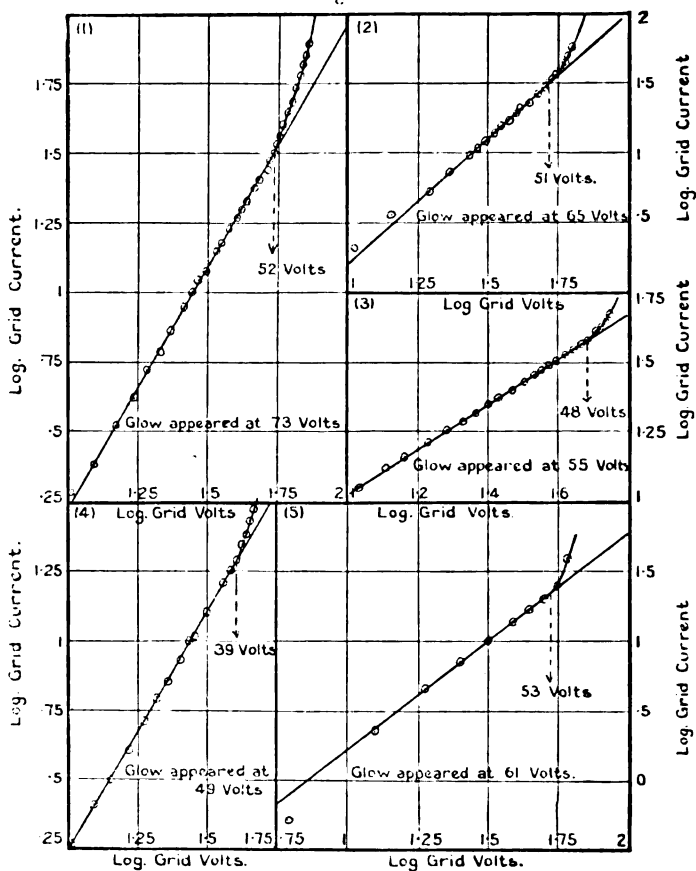


Fig. 6 b.



In general the bend occurs at a higher value for a higher appearing potential. Table V. gives the position of the ionization bend in a series of curves, and in each case the corresponding potential at which the glow appeared. The

TABLE V.

Ionization break. Volts.	Appearing Voltage.
51	63
39	49
52	73
54	—
50	57
53	63
48	55
58	72
49	55
53	57
59	80

General order of pressure ..... .01-.05 mm.

average value for the upper limit lies between 48 and 54 volts; there are two higher values at 58 and 59 volts, corresponding to high appearing voltages, but in both cases the pressure was low. It is impossible to say, from the curves already obtained, whether there is a definite upper limit to the voltage at which ionization takes place, since the position of the bend can be shifted through two or three volts by changes of pressure, filament current, etc.; it would be necessary to perform experiments with a linear source of constant velocity electrons to establish this point. Table V., however, indicates that possibly there is such an upper limit.

When the glow finally did appear, the currents were large: often about 180 milliamperes. Characteristic curves at the same order of pressure for the tube in the ordinary conditions, with or without liquid air near the filament, showed quite a different form of curve (fig. 6c). Even at very low pressures, the potential at which ionization was detectable was much lower than that observed for the "disappeared" state.

(e) The disappearance was much more easily obtained when the level of the liquid air was high round the collecting-tube, and when there was therefore a sharp temperature gradient near the filament. Also the current could be made to increase by pressing cotton-wool soaked in liquid air on to the outside of the main tube next to the upper end of the filament; this sometimes caused an increase of about 10 milliamperes. The cooling was more effective the nearer the cold spot was to the filament.

(f) Before disappearance the glow was much fainter over the liquid air than behind the filament.



(g) With this type of disappearance the secondary glow was never seen.

(h) The "disappeared" state would persist for hours unless the liquid air was removed.

(i) The characteristic curve showed the hysteresis effect in the region of the glow striking potential.

(j) The difference between the currents before and after the disappearance of the glow was greater the greater the ionization; for instance, a current of 100 milliamperes would drop to about 10 milliamperes.

(2) *Absorption of Gas*.—Gas was absorbed into the walls of the tube even when there was no potential on the grid, but this was more marked the greater the ionization. A certain amount was restored on heating to red heat, and, when tested, behaved like ordinary hydrogen. The discrepancy between the amount disappeared and the amount restored was always greater with large ionization currents. The following table gives an example:—

TABLE VI.

Ratio of gas disappeared/gas returned.	Grid volts.	Ionization current. (milliams.)
255/87	up to 75	up to 450
125/71	34	—
67/59	32	30
191/80	up to 80	200

(3) *Fluorescence of the Quartz*.—After experiments in which an intense glow had been in the tube for some time, on switching off the filament the tube glowed with a whitish phosphorescence, and when heated gave out a bright green fluorescence, which was destroyed by heating to red heat and was only recovered by leaving the glow on again. It was an internal effect, and not due to the flame with which the tube was heated, as it also showed on the small quartz tubes covering the electrodes inside the main tube. A similar effect has been noted by other workers with quartz tubes, and has been shown by Ludlam and West\* to be due to small impurities in the quartz, which absorb radiation from a glowing gas and show an accelerated phosphorescence on heating. It was probably strong ultraviolet radiation that was absorbed in this case; as far as could be seen with a direct-vision spectroscope, the spectrum of the fluorescent light was a continuous band in the green.

\* Ludlam and West, 'Nature,' March 15, 1924.

(4) *Return of Pressure.*—The return of pressure on switching off the filament (as with the glass tube (II. 4)) was very marked in the quartz tube. It occurred with or without liquid air on the collecting-tube, and also, though to a less extent, when there was no potential on the grid.

The filament in the quartz tube burnt out, and was replaced by another, arranged so that it was just behind the collecting-tube instead of immediately over it. Though the results observed before were all reproduced, they were on a smaller scale, and the currents were not so large. It was not so easy to get the disappearing glow, and a lower pressure, of the order of .01 mm., was necessary to observe it at the higher voltages. The green fluorescence was not visible, but by this time there was a considerable metallic deposit on the walls.

(5) *Effect of charging the Walls.*—This deposit was examined, and was found to consist in part of a fine layer of tungsten, and in part of a flaky metallic deposit all round the tube just behind the grid. On analysis this proved to be chiefly nickel with perhaps just a trace of mercury. The grid must therefore have been sufficiently hot to drive out any occluded gas. Connexion was made to the deposit by inserting a stranded copper wire with a brush of wires at the end down the outlet tube; the wire was bent so that the brush pressed against the upper wall of the main tube. The end of the wire was sealed in through a T-piece above the outlet tube. The deposit was very uniform, and formed an efficient internal metallic coating. Experiments were then carried out to see how far the foregoing results were affected by a positive or negative potential on the walls.

(a) The return of pressure was not affected by either earthing or putting a negative potential on the walls; it also occurred when the glow was in a "disappeared" state. With a positive potential on the walls, it was shown up to a certain point when the nature of the discharge changed, and nearly all the current went to the walls; on switching off the filament then, the pressure either remained the same or decreased.

(b) Curves were plotted showing the relation between grid current and wall potential, and current to the walls and wall potential, for constant grid potential (fig. 7a).

With the grid above the ionizing potential, as would be expected, one curve is the mirror image of the other. Very little effect is observed on charging the walls negatively; both the grid and wall currents have practically constant values, the latter negative, (observed by interchanging the

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grid and wall leads and reversing the connexions to the milliammeter). The negative current is obviously due to the accumulation of positive ions. The kink in the curve at 0 volts shows the potential acquired by the insulated walls. When the walls are charged positively, with increasing charge they take more and more positive current from the grid. The potential on the insulated walls may be read off the curve by drawing a horizontal line from the point giving the current for insulation to the curve on the positive side,

Fig. 7 a.

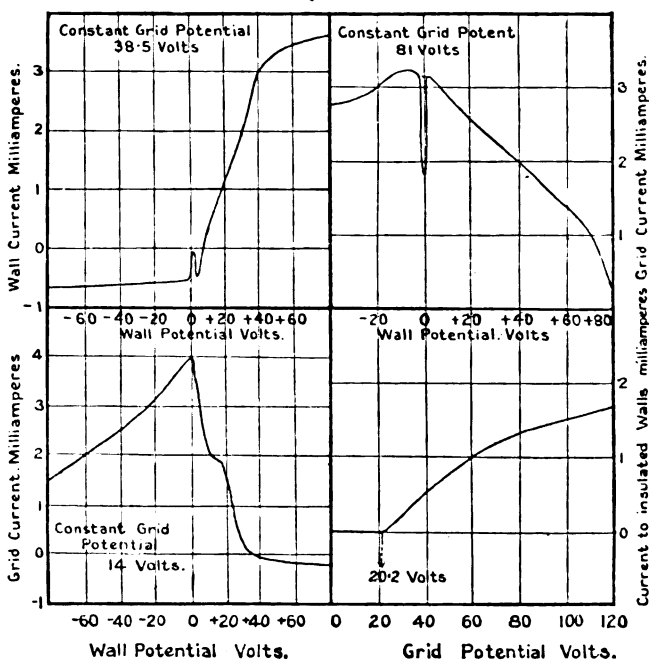


Fig. 7 b.

Fig. 7 c.

and the point at which the curve cuts this line corresponds to a certain potential, which is also that of the insulated walls. The same type of curve was shown whether liquid air was on or off the collecting-tube.

With the grid below the ionizing potential, the tube acts as a three-electrode valve. The curves are of the form shown in fig. 7 b. The grid current gradually increases as the wall potential is increased from a negative value. With a positive potential on the walls, the grid current approaches

a saturation value, but decreases again at about 19 volts, owing to the production of positive ions. A second saturation is shown later; the grid current is then negative, as positive ions are driven into it.

The apparatus was arranged at one time so that the potential of the insulated walls could be read for increasing grid potential. Fig. 7c shows this relation. There is zero current to the walls till ionization takes place. The point where the curve breaks away from the line of zero current indicates the potential at which positive ions appear. A current of .001 milliamperes could be detected by the milliammeter, and a sensitive galvanometer could be deflected by much less. With sufficient increase of grid potential, the current to the insulated walls and the potential of the walls reached constant values. When the glow was bright and there was a large current to the grid, for instance about 120 milliamperes, the potential of the insulated walls was small, of the order of 2 or 3 volts; when the grid current was small (4 or 5 milliamperes) the potential of the insulated walls was large (15, 20, or even on one occasion 40 volts); the grid voltage in the latter case was 80 volts. The potential on the walls was increased by putting liquid air on the collecting-tube. Just before the glow disappeared, the wall potential fell slowly and then gave a jump to zero.

(c) Earthing the walls or charging them negatively did not prevent the disappearing glow, nor did a positive charge up to a certain limit at which a very large proportion of the electrons went to the walls instead of the grid. If the glow was first made to disappear and a sufficient positive potential then put on the walls, it would reappear, and on removing the lead from the walls, the grid current increased above its former value.

(6) *Spectroscopic Observations.*—Rough observations were made on the spectrum of intense glows which accompanied large currents at low voltages; a Hilger spectroscope was used. The most prominent lines in the secondary spectrum were those placed by Fulcher\* in Group I. of his classification—those which do not show the Zeeman effect. No photographs have yet been taken.

(7) *Liberated Gas.*—The products condensed in the collecting-tube by liquid air were again examined. The following methods were used:—

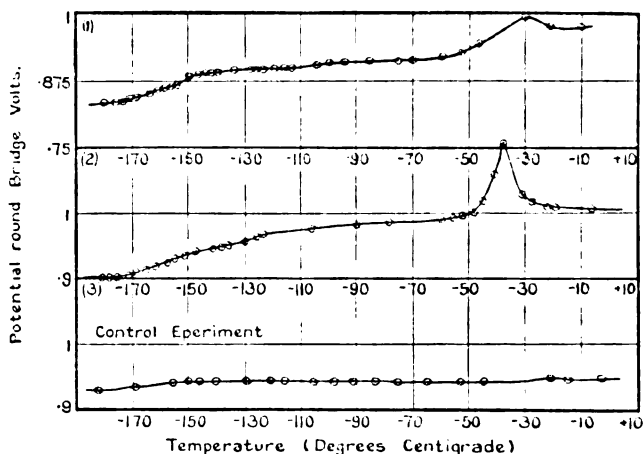
(a) On sparking the liberated gas in the McLeod gauge, it decreased in volume.

\* Fulcher, *Astrophys. Journ.* xxxvii. p. 65 (1913).

(b) On the examination of the glow spectrum of the liberated gas as it passed the filament, the momentary flash showed bright hydrogen lines and bands, and in the case of the glass tube strong carbon bands as well, but these were not noticeable in the quartz tube.

(c) The gas was also investigated by means of the Pirani gauge\*. An Osram lamp was sealed on to the apparatus near the main tube; the lamp filament formed one of four arms of a Wheatstone bridge. When gas was liberated from the collecting-tube, the resistance of the lamp filament altered, and the balance was regained by adjusting the total potential round the bridge. The temperature of the collecting-tube

Fig. 8.



was roughly determined by means of a direct-reading thermopile inserted in a tube of ether round the collecting-tube, the whole being immersed in liquid air. The temperature was plotted against the total potential round the bridge. When no gas was being given off, the curve had a slight upward slope, since the volume of the collecting-tube was comparable to the volume of the part of the apparatus into which the gas could expand. When gas was given off, the curve rose more steeply till all the particular gas had been given off; it then continued nearly horizontal till the next gas was liberated. The curves obtained with the glass tube were irregular, and showed that several gases were present. The curves for the quartz tube (fig. 8) showed that certainly one, and possibly

\* General Electric Co., Proc. Phys. Sec. 1921, p. 287.

two, non-recondensable gases were present, besides a certain amount of mercury which could not be removed, and was recondensable in the upper liquid-air trap, as the fall at the end of the curve shows. The other product or products were given off between the temperature of  $-174^{\circ}$  and  $-140^{\circ}$  centigrade. The exact temperature could not be determined, as the position of the thermopile varied, and only gave a rough approximation of the temperature of the collecting-tube; also this form of gauge takes about a minute to settle for each reading, so that it is very difficult to get an accurate continuous series. Fig. 8 also shows the results of a control experiment in which ordinary hydrogen in the collecting-tube was warmed up from the temperature of liquid air.

(d) The characteristic curve for the liberated gas was plotted from readings taken in the quartz tube when there was an insulated rod electrode opposite the grid (see below). The curve (fig. 9) was very similar indeed to one taken for hydrogen at very much the same low pressure.

(8) *Effect of extra Electrode.*—Various experiments were performed when the tube had this extra electrode. The main results noted were as follows:—

(a) The currents were not nearly so large as had been observed in the tube before.

(b) At no time was the secondary spectrum any more than faint; the Balmer lines were always the most prominent.

(c) The disappearing glow could not be produced except at very low pressure, when it is probable that there was not enough gas to maintain the ionization current.

(d) The return of pressure with the filament off was unaffected.

(e) The characteristic curve was somewhat altered in form. It showed a sharp rise at about 18 volts, which was marked even at a pressure of  $\cdot 003$  mm.; with the tube in its former condition no noticeable rise could be seen at this order of pressure.

(f) The hysteresis effect was well marked.

#### SUMMARY OF RESULTS.

(1) The cylindrical tube with open grid and no anode is favourable for the production of large currents and glows showing intense secondary spectra; these show a time-effect in their growth to a maximum.

(2) With an optimum spacing of grid wires and in the presence of carbon vapour, the glow shows regular oscillations.

(3) In the presence of carbon vapour, a very large proportion of the hydrogen present can be made to condense at a temperature of liquid air. If carbon is eliminated as far as possible by using a quartz tube etc., a small but definite amount of the hydrogen still condenses, either by itself or in the form of a compound. The liberated gas is non-recondensable and behaves like ordinary hydrogen.

(4) When there is a sharp fall of temperature close to the filament, by suitable treatment the gas in the tube may be brought to a condition where there is no detectable ionization, even though the grid potential is above the ionizing potential of hydrogen. This condition is stable for at least an hour, probably longer. The gas may be brought back to the ionized condition by removing the liquid air or by giving a sufficient positive charge to the walls of the tube.

(5) When the filament is bright, hydrogen is absorbed by the walls whether there is a potential on the grid or not, though more is absorbed in the first case. The absorption also occurs whether the walls are earthed, charged positively or negatively. Only part of the gas is liberated on heating the walls to red heat.

(6) When the walls are insulated they acquire a considerable positive charge, which is greater for small grid currents and less for large grid currents.

(7) On heating the filament there is a decrease in pressure, but there is a certain return of pressure on switching off the filament and allowing the tube to stand for about half-a-minute. This effect is independent of the charge on the walls, the potential on the grid, and the presence of another insulated electrode; provided the nature of the discharge does not change, the magnitude of the effect is in general greater for greater ionization.

(8) The insertion of an insulated-rod electrode opposite the grid modifies the characteristic curves, reduces the currents, and prevents the occurrence of the disappearing glow. It also intensifies the Balmer lines in comparison with the secondary spectrum.

#### DISCUSSION OF RESULTS.

##### (1) *Return of Pressure.*

The pressure changes described in paragraphs II. 4, III. 4, and III. 5a seem to be chiefly an effect due to the filament, since they occur when the grid potential is not on. The pressure is smaller when the filament is glowing than when it is cold, and this probably indicates absorption of gas by the

hot filament with subsequent re-emission when the filament current is cut off. This may be associated with the fall of current from the initial value observed when the filament is switched on, if there is a sufficient potential on the grid to make a considerable quantity of positive ions. There is at first a definite decrease of current from the initial value, independent of any subsequent growth; the fall-back can be reproduced after allowing the tube to stand for a short time with the filament off.

It appears likely that this is due to the formation of an endothermic compound of hydrogen and tungsten which depresses the emission of the filament. Such a compound might be quite stable at 2500° K. and extremely unstable at ordinary temperatures. Langmuir\* states that all the atomic and 65 per cent. of the molecular hydrogen which strikes a heated tungsten filament is absorbed by it, and that further dissociation of the hydrogen takes place within the filament. The increase of pressure occurs more readily when there has been a positive potential on the grid sufficient to ionize the hydrogen, so that probably hydrogen ions ( $H^+$  or  $H_2^+$ ) combine with tungsten more readily than neutral hydrogen molecules. The electric field in the tube will cause the filament to be bombarded by positive ions. The only condition so far observed under which the return of pressure does not occur, is when there is a large positive potential (considerably\* larger than the grid potential) on the walls of the tube. In this case the grid current has either a negative or a very small positive value, which indicates that positive ions are being driven into it. Normally the field in the tube drives the positive ions into the filament, but under these conditions, since the grid has a much larger surface area and is at a considerably lower potential than the walls, it probably collects most of the positive ions and acts as a screen to the filament. Calculation of the mean free path in hydrogen showed that it was of the order of the distance between the filament and grid (about 1.5 mm.) at a pressure of about .08 mm. The mean free path of an electron is certainly greater; and as the experiments were generally carried out at a pressure less than .08 mm., the grid would effectively screen the filament from most of the positive ions formed.

## (2) *Nature of the liberated Gas.*

In the glass tube there can be little doubt that the gas released when the liquid air is removed from the collecting-tube consists largely of compounds containing carbon and

\* Langmuir, Journ. Amer. Chem. Soc. xxxvii. p. 451 (1915).

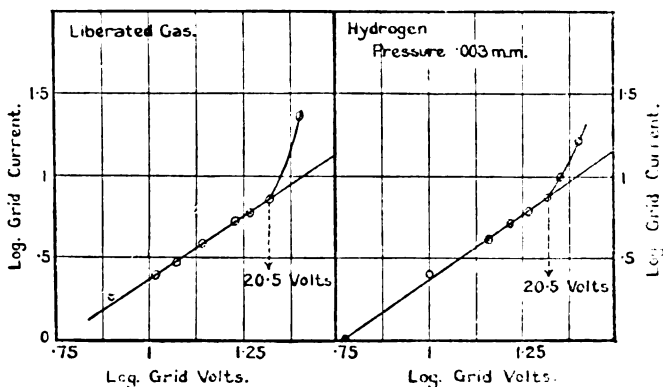


hydrogen. This is shown by (a) the presence of strong carbon-monoxide bands along with hydrogen lines in the spectrum of the gas ; (b) the large, but irregular, increase in volume when the gas is sparked. It seems probable that hydrocarbons would be formed by the action of hydrogen ions on carbon compounds from the glass, and it is known that such compounds as ethane are decomposed by an electric discharge.

The curve obtained with the Pirani gauge shows that a number of different substances are present in the collecting-tube, and that these substances evaporate one by one as the tube is allowed to warm up after the liquid air is removed.

In the quartz tube it is unlikely that carbon compounds can exist in appreciable quantities after the tube has been in

Fig. 9.



use for some time. The quartz was heated red hot by a blow-pipe each morning before experiments were started, and the liberated gas was pumped out by a Gaede pump and by charcoal and liquid air. The electrodes constituted the only other available source of carbon, and these were always at a high temperature when the tube was in use, the grid being kept at red heat by electron bombardment. Any carbon originally present would probably disappear in a few hours under these conditions.

The spectrum of the gas liberated from the quartz tube showed only hydrogen lines and bands, though this by itself cannot be taken as a proof of the absence of carbon. The characteristic curve of the liberated gas closely resembled that obtained under similar conditions with hydrogen at low pressure (fig. 9). Also the liberated gas, like hydrogen in

control experiments, showed a diminution in volume when sparked in a quartz capillary tube, whereas hydrocarbons give a large increase in volume. The Pirani gauge experiments showed that the gas in the collecting-tube came off when the temperature was between  $-174^{\circ}\text{C.}$  and  $-140^{\circ}\text{C.}$ , and was non-recondensable in liquid air. It therefore seems very probable that the liberated gas is hydrogen, and three possible hypotheses suggest themselves:—

(a) That hydrogen in the atomic state is absorbed by the walls of the collecting-tube. This would correspond to Langmuir's \* NR gas.

(b) That a condensed form of hydrogen, such as  $\text{H}_3$ , is present in the collecting-tube, stable at the temperature of liquid air, but dissociating at higher temperatures.

(c) That active hydrogen forms a compound with mercury, nickel, or tungsten, and that this compound is unstable except at very low temperatures.

The fact that the gas is non-recondensable is satisfied by all three possibilities.

The first hypothesis does not seem consistent with the form of the Pirani gauge curves. If the gas was absorbed by the walls of the collecting-tube, the amount absorbed would be greater the lower the temperature. Some gas would be given off directly the liquid air was removed, and the curve would immediately show an upward slope; whereas the initial part of the curve is nearly horizontal, and the spot of light on the galvanometer scale was practically steady until the thermopile, which was inserted next to the coldest part of the collecting-tube, read about  $-170^{\circ}\text{C.}$  The spot of light then moved on the scale, and the curve took a definite upward bend. On either of the other two hypotheses, the liberation of the gas on removal of the liquid air is a dissociation, and not simple evaporation. The glow spectrum of the liberated gas, obtained as it passed the filament, showed at first marked hydrogen secondary lines and bands; these gradually faded away, leaving the Balmer lines most prominent. This change may have been simply due to lowering of pressure as the gas diffused into the other parts of the apparatus, but it is unlikely that atomic hydrogen would show a marked secondary spectrum immediately on liberation into a practically evacuated tube. Also the pressure during the experiments was higher than that ( $.001$ – $.01$  mm.) at which Langmuir found that the atomic form of hydrogen (NR gas) was present in large quantities near a glowing filament, so that these conclusions are not necessarily in conflict with his.

\* Langmuir, Journ. Amer. Chem. Soc. xxxiv. p. 860 (1912).

It does not seem possible to differentiate between hypotheses (b) and (c) without further data.

(3) *The disappearing Glow.*

Any theory of the disappearing glow must account for (a) the necessity of having liquid air close to the filament; (b) the step-up process; (c) the marked difference in the potential at which ionization appears in ordinary hydrogen, and in hydrogen in which the glow has been made to disappear; (d) the time factor.

The gradual hardening-up of the tube during the discharge is not capable of accounting for (a) or (c), since ordinary hydrogen at approximately the same pressure behaves normally (fig. 6 a). The discrepancy between the two voltages at which ionization takes place in the two cases is much too great to be accounted for by changes of pressure, filament current, etc. The ionization potential observed in the ordinary case is probably the critical potential that exists at about 16 volts, since the fall of potential down the filament was from 4 to 6 volts. The corrected potential at which the abnormal gas is ionized would be roughly between 42 and 51 volts. Smyth\* has deduced from his experiments that under certain conditions  $H_2^+$  is formed at 16.5 volts and is not accompanied by dissociation. Horton and Davies† also assign a critical potential at 15.9 volts to the molecule, though Olmstead‡ considers that the molecule is dissociated and one atom ionized at this point. It seems, however, quite certain that we are here dealing chiefly with a molecular action. The growth of the glow is accompanied by a gradual intensification of the secondary spectrum. Other workers have found similar phenomena at liquid-air temperatures, and all ascribed it to some kind of molecular action §.

The change in the form of the characteristic on inserting a third insulated electrode shows that the latter modifies the field in the tube and shifts the region where  $\frac{dV}{dx} = 0$  nearer the filament, thereby reducing the negative space-charge; with the tube in this condition it was impossible to obtain the large currents and disappearing glow.

\* Smyth, Proc. Roy. Soc. cv. pp. 116-128 (1924).

† Horton & Davies, Phil. Mag. Nov. 1923.

‡ Olmstead, Phys. Rev. p. 613 (1922).

§ Wendt & Landauer, Journ. Amer. Chem. Soc. xlv. p. 510 (1922); Lemon, Astrophys. Journ. xxxv. p. 109 (1912).

We have therefore, as essentials for the production of the abnormal condition, (a) the presence of liquid air near the filament, (b) a very dense electron stream resulting in a large negative space-charge, (c) a considerable time factor.

These conditions result in the growth of very large currents, sufficient to maintain the grid at red heat and to cause a large amount of nickel to sputter on the walls, and the gradual intensification of the secondary spectrum, especially the Fulcher Group I. bands. This state must first be acquired at a low potential, but may be observed at a high potential by a step-up process; it does not occur if the high potential is applied in the first place.

We put forward the following tentative explanation:—

The conditions seem favourable for the formation of some substance with a large molecule, such as either  $H_3$  or a compound of hydrogen with mercury, nickel, or tungsten, or they may all be formed. The very dense electron stream would increase the chances of production of negative atoms or molecules, and the presence of these would probably favour the formation of such compounds. The gradual growth of the current and the time-effect involved indicate that the chief action of the liquid air is to slow down the heavy positive ions which tend to collect near the filament and in some way form larger neutral molecules by combination with negative ions, the process of accumulation taking a considerable time. This will reduce the partial pressure of  $H_2$  so that when the grid potential is momentarily disconnected and then put on again, the glow is unable to start up until the potential has been raised a few volts. The heavy neutral molecules continue to accumulate, and the partial pressure is again reduced. In this way the appearing voltage of the glow is gradually stepped up, until the accumulation is very considerable. This idea of the gradual reduction of the partial pressure of  $H_2$  is supported by the fact, frequently observed, that when the glow has been on for some time in the quartz tube, the portion of the glow over the liquid air just in front of the grid is definitely fainter than the part at the back of the tube behind the electrodes. When the step-up process has been accomplished, the gas is then in the curious condition in which the characteristics show no evidence of ionization below 42–51 volts.

It seems that there are two possible explanations of the high ionizing potential:—

(a) The substance which accumulates is a neutral molecule which possesses considerable stability, and the upper limit of the values found for the high ionizing potential represents

the voltage required to decompose it, when the partial pressure of  $H_2$  is too low to produce an appreciable number of positive ions at a lower voltage.

(b) In some way the emission of the filament is depressed, either by increasing the negative space-charge or by action on the filament itself, and that to overcome this condition, electrons of much higher velocity are required. It appears that the only way of increasing the negative space-charge would be by the accumulation of a large number of negatively-charged molecules or atoms which are known to be sometimes present in hydrogen subjected to discharges of various kinds\*. However, the abnormal condition is not destroyed by switching off the filament; so that it does not seem likely that this hypothesis is the right one. It also seems improbable that the emission of the filament can be seriously impaired by chemical action, since there are enough electrons emitted to give considerable grid currents, up to 30 milliamperes, before there is any detectable ionization, when the tube is in the abnormal state. We therefore conclude that (a) is the more likely explanation.

It remains to decide whether the large neutral molecule is an aggregate of hydrogen, such as  $H_3$ , or a compound of hydrogen with one of the metals present—nickel, mercury, or tungsten.

The abnormally large currents are similar to those obtained by Compton and Duffendack† in their experiments on nitrogen. They found a very active form of nitrogen at 70 volts or more; this condition was accompanied by a large clean-up and by very big currents up to 4 amperes, which caused the appearance of globules of nickel; the electrodes finally fused. They suggest the possibility that nickel is a catalytic agent in an action of this sort. Gauzer‡ finds indication of the existence of a nickel-hydrogen complex by observation of the critical potentials of hydrogen in the presence of nickel, and so accounts for the catalytic influence of nickel in the chemical reactions of hydrogen.

Compton and Turner§ have found spectroscopic evidence of the existence of a mercury hydride in a discharge-tube containing mercury and hydrogen.

It seems most probable that the gas which collects in the liquid air is to be identified with some kind of hydrogen-metal

\* J. J. Thomson, 'Rays of Positive Electricity'; Foote & Mohler, Bureau of Standards, 400, p. 669, vol. xvi.

† Compton & Duffendack, *Phys. Rev.* May 1924, p. 85.

‡ Gauzer, *Journ. Amer. Chem. Soc.* March 1924.

§ Compton & Turner, *Phil. Mag.* August 1924.

compound, and is stable at low temperatures, but dissociates spontaneously when the temperature is raised, for the gas which is liberated appears to be ordinary hydrogen. It is not likely that an unstable compound of this description would show the definite ionization effects seen in the tube; also gas is condensed in the collecting-tube in the absence of the disappearing glow effect. It therefore seems reasonable to conclude that several actions occur in the tube simultaneously:—

(a) Hydrogen acts on the filament to form an endothermic compound with tungsten, stable at high temperatures. (Return of pressure.)

(b) The conditions favour the production of negative ions, which combine with

(1) one or several of the metals present, to form a compound or compounds stable at liquid-air temperature but unstable at ordinary temperatures (possibly identical with (a));

(2) positive hydrogen ions, to form a large hydrogen molecule such as  $H_3$ , which is not ionized until the grid potential reaches a value between 42 and 51 volts. On this view,  $H_3$  must be considerably stable under these conditions, and must be more difficult to ionize than  $H_2$ . This is surprising, but is in accordance with the deductions of H. S. Allen\* from his static models of  $H_2$  and  $H_3$ . He calculates that a potential of 46 volts would be necessary for the complete disintegration of a molecule of  $H_3$ . Smyth†, in his recent work on positive rays, has found under certain conditions a preponderance of  $H_2^+$  ions, and at the same time distinct evidence of a considerable number of  $H_3^+$  ions.

#### (4) Oscillations.

It does not seem possible at present to find a satisfactory explanation of the oscillations with only the results we have so far obtained; further investigations are necessary. It is certain that large quantities of carbon compounds are in the oscillating-tube, since they show their presence in the other glass tube by their condensation in liquid air and decomposition by a high voltage, giving an increase in gas-pressure (Table III.). The slow oscillation at low voltage would suggest that it was due to the periodic formation and decomposition of such substances, but it is difficult to reconcile this hypothesis with the very rapid oscillations at high

\* H. S. Allen, Proc. Roy. Soc. Edin. xliii. No. 13 (1922-23).

† H. D. Smyth, 'Nature,' July 26th, 1924.

voltage. The latter suggest some kind of oscillation due to the fall of potential between the grid and filament as a result of the large current, but again it is difficult to apply such a hypothesis to a slow oscillation with a period of several minutes, when the glow is already present. It seems necessary to investigate more fully the conditions for the production of these oscillations, and why they were only produced with one set of electrodes. We shall be glad if other investigators can throw light on their mechanism.

Cavendish Laboratory,  
Cambridge,  
August 1924.

XCV. *On the Coefficient of Performance of Refrigerating Machines employing Throttle Expansion.* By ALFRED W. PORTER, D.Sc., F.R.S., F.Inst.P., Professor of Physics in the University of London\*.

WHEN comparison is made between two cases of mechanical refrigeration in one of which the cooling is produced by cylinder expansion and in the other by throttle expansion but in which all else is the same in both, the coefficient of performance is less in the throttle case than in the other for two reasons :

- i. More work is required to keep the fluid in circulation.
- ii. Less heat can be removed from the cold stores.

This can be explained by aid of pressure-volume and temperature-entropy diagrams.

Sketch diagrams are shown in figs. 1 and 2. The points in fig. 2 which correspond to points in fig. 1 are marked with accented letters.

When cylinder expansion is used the refrigeration per cycle is  $\frac{DA}{EF} \times \text{latent heat at } T_2$  or  $D'A' \times T_2$  where  $D'$  is vertically below  $C'$ ; while the work required for circulation is area DABC or  $D'A'B'C'$ .

Hence the coefficient of performance is

$$\frac{D'A' \times T_2}{\text{Area } D'A'B'C'}.$$

If, however, expansion through a throttle takes place at

\* Communicated by the Author.

C the state after expansion is indicated by a point  $H'$  (or  $H$ ) where  $H'$  and  $H$  are to the right of  $D'$  and  $D$ , since the entropy increases in the expansion, although the change is

Fig. 1.—Pressure-volume diagram.

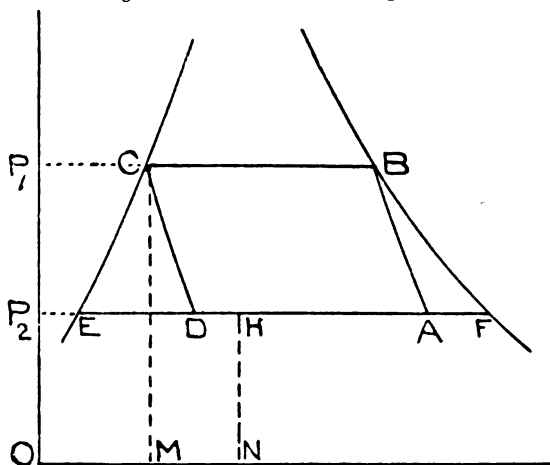
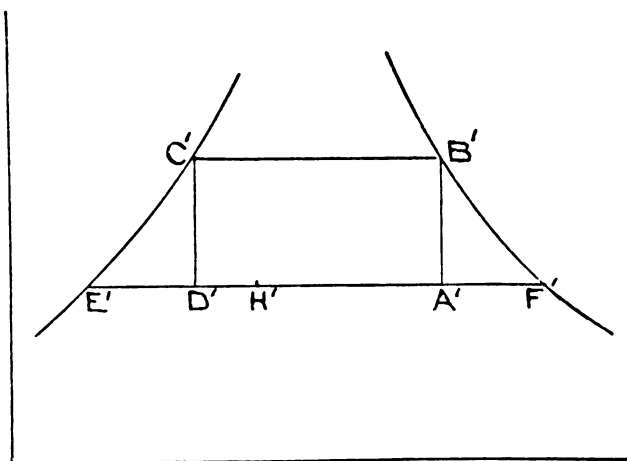


Fig. 2.—Temperature-entropy diagram.



adiabatic, by an amount calculable from the frictional heat in the throttle. The refrigeration per cycle is now only

$$\frac{HA}{EF} \times \text{latent heat at } T_2$$

$$\text{or } H'A' \times T_2.$$



It is not quite so obvious how the work of circulation is increased, but an examination of the heat entry round the cycle will make it clear.

Let the heat given out to the condenser in each case be  $H_1$  while the refrigeration is  $H_2$  in the cylinder case and  $H_2'$  when the throttle is used. Then by applying the law of the conservation of energy to the complete cycle we have, since the paths AB and CD or CH are adiabatic :

$$\text{Cylinder case: } W = \text{work of circulation} = H_1 - H_2.$$

$$\text{Throttle case: } W' = \text{,, ,, ,,} = H_1 - H_2'.$$

But  $H_2'$  being less than  $H_2$  it follows that  $W'$  is greater than  $W$  by an equal amount. If this excess  $W' - W = w$  (say) we have

	Cylinder case.	Throttle case.
Coeff. of performance ...	$\frac{H_2}{W}$	$\frac{H_2 - w}{W + w}$ .

Thus it appears that  $w$  plays a two-fold function detrimental to effectiveness.

#### *Calculation of $w$ .*

The principal part of this note is concerned with the exact calculation of  $w$ . It is usually stated that the point H' can be determined by making  $D'H' \times T_2$  equal to the approximately triangular area  $E'C'D'$ . In a contribution which I made to Hal Williams' 'Mechanical Refrigeration' (Whittaker & Co., 1903) I indicated that this is not correct and may only give about half the true value of the correcting term  $w$ . No proof was given of this and I now supply this proof.

The characteristic of adiabatic throttle expansion is that  $E + pr$  is the same before and after the expansion, where  $E$  is the internal energy,  $p$  the pressure, and  $v$  the specific volume. The external work done in the expansion is therefore  $p_2v_2 - p_1v_1$ . In the cylinder case, the external work is represented by the area underlying the path traversed on the  $p.v$  diagram. Hence

	External work.
Cylinder ...	CDHNM
Throttle ...	$p_2v_2 - p_1v_1 = P_2HNO - P_1CMO$ .

The difference  $w$  equals

$$CDHNM + P_1CMO + ONHP_2 = P_1CDP_2.$$

Now this is greater than ECD (the value usually taken) by the area  $P_1CEP_2$ . Hence to determine the point  $H_1$  on the

entropy diagram we must make  $D'H' \times T_2 = \text{area } P_1CDP_2$  on the  $p-v$  diagram. This area is bounded on one side by the cylinder adiabatic CD. To avoid calculating the form of such an adiabatic the area can be represented as

$$P_1CEP_2 + CDE.$$

But  $CDE = C'D'E'$  because both these areas correspond to the work done in the same possible reversible cycle. But the path  $C'D'$  on the entropy diagram is vertical and consequently the point  $D'$  is easily determined.

The area  $P_1CEP_2$  must however be obtained from a  $p,v$  chart. Using Behn's values for the border curve of carbon dioxide I obtain the following values for the area, reckoning from  $0^\circ \text{F.}$  as origin. The values are given both in British and in C.G.S. units.

Area  $P_1CEP_2$ .

Temp. F.	B.T.U. lb.	Temp. C.	Gram. Cal. gram.
70	1.85	20	.98
60	1.48	15	.81
50	1.19	10	.67
40	.87	5	.50
32	.65	0	.35
30	.61	- 5	.22
20	.36	- 10	.12
10	.15	- 15	.06
0	0	- 20	0

The area  $P_1CEP_2$  corresponding to any particular range of temperature is obtained from the above by taking the difference of the values for the extreme temperatures. For example :—

$$\left. \begin{array}{l} \text{Condenser temp. ... } 70^\circ \text{F.} \\ \text{Refrigerator ,, ... } 5^\circ \text{F.} \end{array} \right\} \begin{array}{l} \text{Area} = 1.85 - .075 \\ = 1.775 \text{ B.T.U. per lb.} \end{array}$$

$$\left. \begin{array}{l} \text{Condenser temp. ... } 20^\circ \text{C.} \\ \text{Refrigerator ,, ... } -15^\circ \text{C.} \end{array} \right\} \begin{array}{l} \text{Area} = .98 - .06 \\ = 0.92 \text{ gr.cal. per gr.} \end{array}$$

To the value calculated in this way must be added the thermal equivalent of the area  $C'D'E'$  which is the area usually taken into account. From the temperature-entropy chart of Jenkins and Pye (Trans. Roy. Soc. Lond. A, 215. p. 361) this can be calculated with sufficient accuracy for any

*Phil. Mag.* S. 6. Vol. 48. No. 287. Nov. 1924. 3 X

fall of temperature lying between  $+20^{\circ}\text{C.}$  and  $-20^{\circ}\text{C.}$  (or  $+70^{\circ}\text{F.}$  and  $0^{\circ}\text{F.}$ ) by the following simple formulæ:

$$\text{Area } C'D'E' \begin{cases} \text{in cal. per gram ... } .00106 \text{ (fall of temp. C.)}^2. \\ \text{in B.T.U. per lb. . } .00059 \text{ (fall of temp. F.)}^2. \end{cases}$$

*Example:*

Condenser temp.  $70^{\circ}\text{F.}$  Refrigerator temp.  $5^{\circ}\text{F.}$

Area  $P_1CEP_2$  .....  $1.775$  B.T.U. per lb.

Area  $C'D'E'$  .....  $2.493$  „ „

Total  $w$  .....  $4.268$

$$\text{Cylinder coefficient of performance } \frac{460 + 5}{65} = 7.15,$$

$$\text{or } \frac{H_2}{W} = \frac{53}{7.41} = 7.15,$$

as read off an entropy chart.

In the case of throttle expansion we have instead

$$\text{coeff. of performance} = \frac{H_2 - w}{W + w} = \frac{53 - 4.27}{7.41 + 4.27} = 4.2.$$

The usual calculation would give  $5.1$  instead, that is  $21$  per cent. in excess of the true value.

**XCVI. Quantum Defect and Atomic Number.—II. The Ionizing Potentials of the Rare Gases and of the Halogen Acids.** By LOUIS A. TURNER, M.A., Ph.D., Charlotte Elizabeth Procter Fellow in Physics, Princeton University\*.

**I**F  $\nu$  is the value of a spectroscopic term, the quantity  $x$  defined by the equation  $\nu = R/x^2$ , where  $R$  is the Rydberg constant, is called the effective quantum number, by analogy with Bohr's theory of the hydrogen atom. If  $n$  be the total quantum number of the electron orbit corresponding to the term, the difference  $n - x = q$  is defined as the quantum defect.

In a previous paper† I have shown that the asymptotic value of this quantum defect, which it approaches for the smaller term values of a series of terms, is a linear function of the atomic number for corresponding series of elements of the same chemical sub-group, provided that the quantum

\* Communicated by the Author.

† Louis A. Turner, Phil. Mag. xlviii. p. 384 (1924).

numbers assigned by Bohr be increased for elements of high atomic number. An approximate relationship of the same sort holds for the quantum defects computed from the largest terms of the series, since these do not differ greatly from the asymptotic value and the deviation is usually in the same direction. These largest term values are the ones, however, which are proportional to the ionizing potentials of the elements considered. The value of  $x$ , the effective quantum number for the largest term, can be computed from the relation  $V_i = 13.53/x^2$ ,  $V_i$  being the ionizing potential, and 13.53 being the value of the Rydberg constant expressed in volts, *i.e.* the ionizing potential of the hydrogen atom.

Recent measurements of the ionizing potentials of the rare gases by Hertz\* and Déjardin† present the opportunity for a further test of the linear relation between the quantum defects. Their results for the ionizing potentials are given in Table I.

TABLE I.  
Ionizing Potentials.

	Hertz.	Déjardin.
Ne.....	$21.5 \pm 0.12$	
Ar.....	$15.3 \pm 0.12$	$15.2 \pm 0.2$
Kr.....	...	$12.7 \pm 0.2$
Xe.....	...	$10.9 \pm 0.2$

The values of  $x$  and  $q$  computed from these data are given in Table II. Bohr's quantum numbers are used for Ne and Ar, but that for Kr has been increased by 1 and that for Xe by 2, in accord with the changes made in the quantum numbers for the neighbouring elements, discussed in the previous paper.

TABLE II.

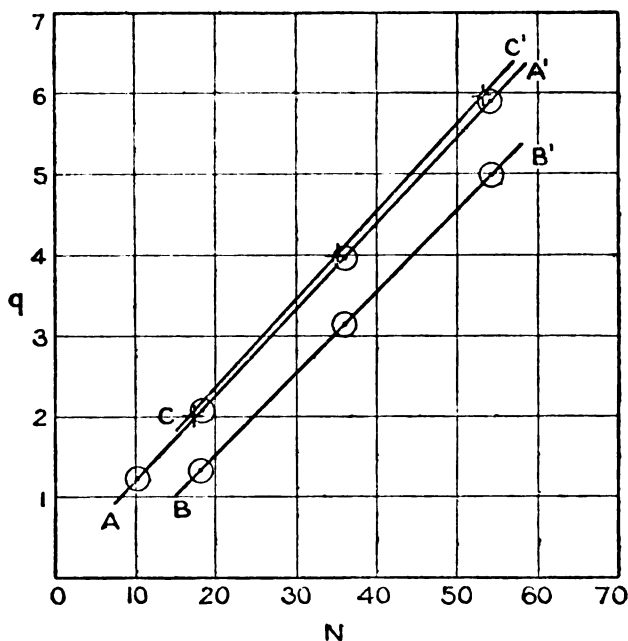
Element.	At. No.	V.	$x$ .	$n$ .	$q$ .
Ne .....	10	$21.5 \pm 0.12$	$0.792 \pm 0.003$	2	$1.208 \pm 0.003$
Ar .....	18	$15.2 \pm 0.2$	$0.942 \pm 0.006$	3	$2.058 \pm 0.006$
Kr .....	36	$12.7 \pm 0.2$	$1.030 \pm 0.009$	5	$3.570 \pm 0.009$
Xe .....	54	$10.9 \pm 0.2$	$1.111 \pm 0.010$	7	$5.889 \pm 0.010$

These values of  $q$  are plotted in the diagram, the line AA' being drawn through them. It has the slope 1.065. The corresponding line obtained from the asymptotic values of the quantum defect of the series of the alkali metals has the slope 1.068. A point corresponding to the ionizing potential of

\* G. Hertz, *Zeit. f. Phys.* xviii, p. 307 (1923).

† G. Déjardin, *C. R.* clxxviii, p. 1069 (1924).

helium does not lie on the line, as would be expected. By extrapolation the ionizing potential of Nt of atomic number 86 can be predicted. The quantum defect predicted is  $9.30 \pm 0.02$ , which corresponds to an ionizing potential of  $27.5 \pm 1.5$  volts if the quantum number is taken to be 10 in agreement with the quantum number of 11 found to be best for the valence electron of Ra. If the quantum number for Nt is taken to be 11 the ionizing potential predicted is  $4.66 \pm 0.11$  volts. An experimental determination of this



quantity is greatly to be desired. It would show whether or not this great extrapolation of the linear relation is valid.

Radiating potentials for these elements have been determined by Hertz \* and Sponer †. The difference between the ionizing potential and a radiating potential of an element gives the value in volts of the spectroscopic term corresponding to the upper level involved in the radiating potential transfer. I have tried to find relations between the quantum defects calculated for these higher levels, but without success. Apparently the transitions are not entirely analogous for all these atoms. It should be noted that experimental errors would introduce very large relative discrepancies in these

\* G. Hertz, loc. cit.

† H. Sponer, *Zeit. f. Phys.* xviii, p. 249 (1923).

term values because of the relatively small differences between the radiating and ionizing potentials.

Déjardin has also determined the critical potential for the appearance of the blue spectrum of Ar, and for the analogous phenomena with Kr and Xe. He attributes the production of these spectra to the double ionization of the atoms. If that hypothesis be correct, the difference between this second critical potential and the ionizing potential of the atom gives the ionizing potential corresponding to the removal of the second electron after the first has already been removed. Table III. gives the data and the quantum defects computed from them. In this computation a value of the Rydberg constant four times that for neutral atoms has been used.

TABLE III.

Element.	Second critical potential.	Second $V_i$	$x$ .	$n$ .	$q$ .
Ar .....	$34.0 \pm 0.5$	$18.8 \pm 0.5$	$1.691 \pm 0.020$	3	$1.309 \pm 0.020$
Kr .....	$28.2 \pm 0.5$	$15.5 \pm 0.5$	$1.866 \pm 0.030$	5	$3.134 \pm 0.030$
Xe .....	$24.2 \pm 0.5$	$13.3 \pm 0.5$	$2.041 \pm 0.046$	7	$4.986 \pm 0.046$

These data are plotted in the figure, the line BB' being drawn through the points. The slope of the line BB' is slightly less than that of AA'. It comes much further below AA' than was the case with similar pairs of lines from the spectrum data discussed in the previous paper.

By extrapolation the second ionizing potential of Ne is predicted to be  $23.7 \pm 1.2$  volts, and the potential for double ionization or appearance of a second spectrum  $45.2 \pm 1.2$  volts. Déjardin points out that this second critical potential is within experimental error equal to 2.22 times the first ionizing potential for Ar, Kr, and Xe. Using that relation, one can predict a value of  $47.7 \pm 0.5$  for Ne. Experiment will have to decide whether either of these predicted values is correct.

C. A. Mackay\* has recently determined values of the ionizing potentials of the halogen acid molecules HCl, HBr, and HI. His data and the quantum defects computed from them are given in Table IV.

TABLE IV.

Molecule.	Atomic No.	$V_i$	$x$ .	$n$ .	$q$ .
HCl .....	17	$13.8 \pm 0.2$	$0.959 \pm 0.008$	3	$2.011 \pm 0.008$
HBr .....	35	$13.2 \pm 0.2$	$1.010 \pm 0.008$	5	$3.990 \pm 0.008$
HI .....	53	$12.8 \pm 0.2$	$1.027 \pm 0.008$	7	$5.973 \pm 0.008$

\* C. A. Mackay, Phil. Mag. xlv. p. 828 (1923).

The quantum numbers are the same as those used for the corresponding rare gases. The values of  $q$  are plotted in the figure and the line  $CC'$  drawn through the points. The fact that the line lies so close to the line  $AA''$  for the noble gases may be taken to be one more bit of evidence favouring the hypothesis that the ionization of one of these molecules consists in the removal of one of the electrons of the halogen atom rather than the splitting up of the molecule into a positive H ion and a negative halogen ion. By extrapolation the ionizing potential of HF is computed to be  $17.9 \pm 0.5$  volts.

### Summary.

It is shown that there is a linear relation between the atomic number and the quantum defects computed from the ionizing potentials of the rare gases, from the second ionizing potentials of the rare gases, and from the ionizing potentials of the hydrogen halide molecules.

The following critical potentials are predicted on the basis of these relations: ionizing potential of Nt,  $27.5 \pm 1.5$  volts; appearance of a "blue" spectrum of Ne,  $45.2 \pm 1.2$  volts; ionizing potential of HF,  $17.9 \pm 0.5$  volts.

Palmer Physical Laboratory,  
Princeton, New Jersey, U.S.A.  
May 28, 1924.

XCVII. *The Effect of a Hole in a Bent Plate.* By W. G. BICKLEY, M.Sc., Lecturer in Mathematics, Battersea Polytechnic\*.

### 1.

IN a recent paper † the effect of a circular hole in a tension member on the distribution of stress is studied experimentally, and it is found that the stresses are considerably enhanced (to about three times the average) at points on the boundary of the hole. In an appendix, a mathematical investigation, limited to the case of an infinitely wide plate, is given, and the experimental results are in close agreement with this, notwithstanding the use of members of finite width. It occurred to the author that a corresponding mathematical investigation of the stresses near a hole in a *bent* plate might also be of some importance as similarly enhanced values of the stresses are to be expected, and some indication of their amount would be obtained. The present paper contains the results of this investigation.

\* Communicated by the Author.

† Coker, Chakko, and Satake, Trans. Inst. of Engineers and Ship-builders in Scotland, 1919.





These formulæ assume that the plate is bent to a state of "generalized plane stress," i. e. that  $\hat{z}z$  vanishes everywhere, and that  $\hat{r}z$  and  $\hat{\theta}z$  vanish at the surface,  $z = \pm h$ . They are not sufficiently general to ensure that the cylindrical boundary is *entirely* free from stress; but these residual stresses are small, and it is possible to obtain a solution which makes the resultant force and couple on any small element of the boundary, standing on an arc  $\delta\theta$ , vanish. To secure this, the boundary conditions are

$$\left. \begin{aligned} G &= 0, \\ N - \frac{1}{r} \frac{dH}{d\theta} &= 0. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (2.4)$$

If the plate is complete, and bent so that the curvature of the  $x$  axis is  $k$ , the  $y$  axis will, in the absence of any bending couple in the  $yz$  plane, have an "anticlastic" curvature  $\sigma k$ . ( $x$  and  $y$  are rectangular coordinates.) We shall then have for  $w$  the formula

$$\left. \begin{aligned} w_1 &= \frac{1}{2}k(x^2 - \sigma y^2) \\ &= \frac{1}{4}kr^2\{(1 - \sigma) + (1 + \sigma)\cos 2\theta\}, \end{aligned} \right\} \quad . \quad (2.5)$$

and then

$$\hat{x}x = -kEz, \quad \hat{y}y = 0 = \hat{y}x,$$

so that the maximum tensile or compressive stress is  $kEh$ . The contour lines of the bent middle surface given by (2.5) are a family of hyperbolas with the common asymptotes  $x = \pm \sqrt{\sigma}y$ .

We may also consider the case of a plate bent into a cylinder of curvature  $k$ , in which case

$$w_1 = \frac{1}{2}kx^2 = \frac{1}{4}kr^2(1 + \cos 2\theta). \quad . \quad . \quad . \quad (2.51)$$

This necessitates a couple in the  $yz$  plane as well as in the  $xz$  plane. Both cases may be included in the formula

$$w' = \frac{1}{4}kr^2(\alpha + \beta \cos 2\theta). \quad . \quad . \quad . \quad (2.52)$$

### 3.

Denoting the radius of the hole by  $a$ , we have a solution of 2.1 which tends to 2.52 when  $r$  is large,

$$\begin{aligned} w &= w_1 + w_2 \\ &= \frac{1}{4}k \left[ \alpha r^2 + \Lambda a^2 \log r + u + \cos 2\theta \left( \beta r^2 + C a^2 + F \frac{a^4}{r^2} \right) \right], \\ &\quad . \quad . \quad . \quad . \quad (3.1) \end{aligned}$$

from which we derive, by equations 2.3 ...

$$G = -\frac{1}{4}kD \left[ \alpha(1-\sigma) - (1-\sigma)A \frac{a^2}{r^2} + \cos 2\theta \cdot \left\{ 2\beta(1-\sigma) - 4C \left( \sigma \frac{a^2}{r^2} + \frac{3(8+\sigma)}{5} \frac{h^2 a^2}{r^4} \right) + 6F(1-\sigma) \frac{a^4}{r^4} \right\} \right], \quad (3.21)$$

$$N - \frac{dH}{r \cdot d\theta} = \frac{1}{4}kD \frac{\cos 2\theta}{r} \left[ 4\beta(1-\sigma) - 4C \left\{ (3-\sigma) - \frac{6(8+\sigma)}{5} \frac{h^2 a^2}{r^4} \right\} - 12F(1-\sigma) \frac{a^4}{r^4} \right]. \quad (3.22)$$

The identical vanishing of these when  $r=a$  leads to:—

$$\left. \begin{aligned} 2\alpha(1-\sigma) - (1-\sigma)A &= 0, \\ 2\beta(1-\sigma) \\ -4C \left\{ \sigma + \frac{3(8+\sigma)}{5} \frac{h^2}{a^2} \right\} + 6F(1-\sigma) &= 0, \\ 4\beta(1-\sigma) \\ -4C \left\{ (3-\sigma) - \frac{6(8+\sigma)}{5} \frac{h^2}{a^2} \right\} - 12F(1-\sigma) &= 0. \end{aligned} \right\} \quad (3.31)$$

Solving these, we obtain:—

$$\left. \begin{aligned} A &= \frac{2\alpha(1+\sigma)}{1-\sigma}, \quad C = \frac{2\beta(1-\sigma)}{3+\sigma}, \\ F &= -\frac{\beta(1-\sigma)}{3+\sigma} + \frac{4\beta(8+\sigma)}{5(3+\sigma)} \frac{h^2}{a^2}. \end{aligned} \right\} \quad (3.32)$$

Thus the displacement due to the hole is:—

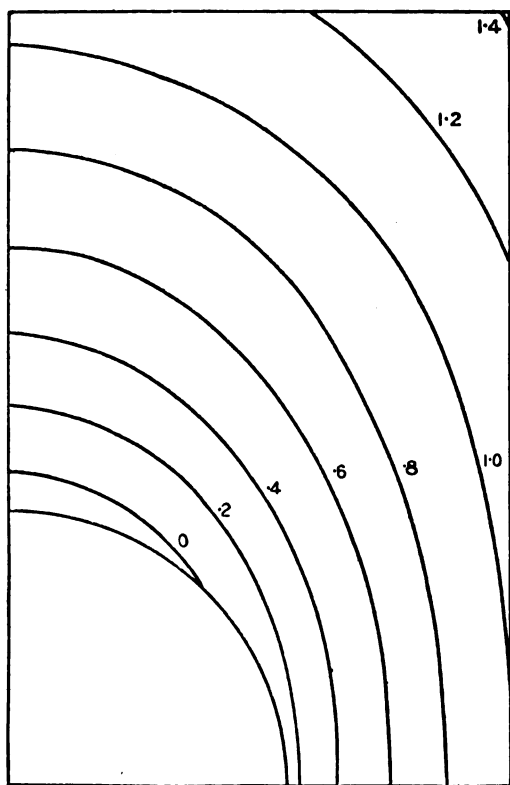
$$w_2 = \frac{1}{4}k \left[ \frac{2\alpha(1+\sigma)}{1-\sigma} a^2 \cdot \log r/a + \left\{ \frac{2\beta(1-\sigma)}{3+\sigma} a^2 - \frac{\beta(1-\sigma)}{3+6} \frac{a^4}{r^2} + \frac{4\beta(8+\sigma)}{5(3+\sigma)} \frac{h^2 a^2}{r^4} \right\} \cos 2\theta \right]. \quad (3.4)$$

Some concern may be felt upon noticing that this makes  $w_2$  infinite at infinity; but a moment's reflexion will show that our formula also makes  $w_1$  infinite there, and that  $w_2$  is small compared with  $w_1$ , for moderate or large values of  $r/a$ ; the formula may be relied upon near the hole, and the stresses derived from it accepted as valid.

By means of this formula, the "relative contours" ( $w_2 = \text{constant}$ ) may be plotted, and they are given in figs. 1 and 2 for the anticlastic and cylindrical cases respectively. The value of  $\sigma$  used in the calculations is 0.28 (*i.e.* a common value for steel), and the unit chosen is the displacement at

$(a, 0)$  in the absence of the hole,  $\frac{1}{2}ka^2$ . The actual contour lines,  $w = \text{constant}$ , are given in figs. 3 and 4 respectively, and the values of  $w$  along the  $x$  and  $y$  axes are plotted in fig. 5. In the last, curves I. are for a complete plate, II. for the anticlastic case, and III. for the cylindrical case.

Fig. 1.



“Relative” contours near a hole in a plate bent anticlastically.

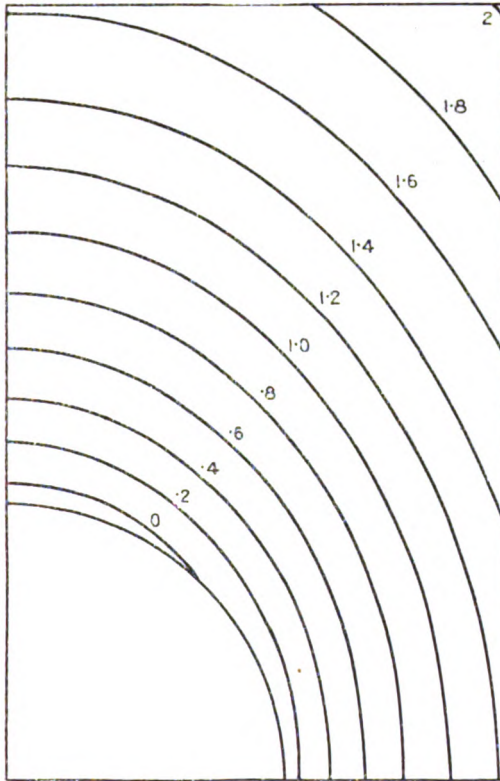
## 4.

We now turn to the consideration of the stresses as calculated from these displacement formulæ. For the anticlastic case, using the appropriate values of  $\alpha$  and  $\beta$  in (3.4) and inserting in equations (2.2) ...., we get

$$\begin{aligned} \hat{r}r = -kEz \left[ \frac{1}{2} \left( 1 - \frac{a^2}{r^2} + \cos 2\theta \left\{ \frac{1}{2} - \frac{2\sigma}{3+\sigma} \frac{a^2}{r^2} \right. \right. \right. \\ \left. \left. \left. - \frac{3(1-\sigma)}{2(3+\sigma)} \frac{a^4}{r^4} - \frac{6(2-\sigma)}{3+\sigma} \frac{a^2}{r^4} \left( \frac{h^2}{5} - \frac{z^2}{3} \right) \right\} \right] \right], \quad (4.11) \end{aligned}$$

$$\widehat{\theta\theta} = -kEz \left[ \frac{1}{2} \left( 1 - \frac{a^2}{r^2} \right) - \cos 2\theta \left\{ \frac{1}{2} + \frac{2}{3+\sigma} \frac{a^2}{r^2} + \frac{3(1-\sigma)}{2(3+\sigma)} \frac{a^4}{r^4} + \frac{6(2-\sigma)}{3+\sigma} \frac{a^2}{r^4} \left( \frac{h^2}{5} - \frac{z^2}{3} \right) \right\} \right], \quad (4.12)$$

Fig. 2.



"Relative" contours near a hole in a plate bent into a cylinder.

$$\widehat{r\theta} = kEz \cdot \sin 2\theta \left[ \frac{1}{2} - \frac{1-\sigma}{3+\sigma} \frac{a^2}{r^2} + \frac{3(1-\sigma)}{2(3+\sigma)} \frac{a^4}{r^4} + \frac{6(2-\sigma)}{3+\sigma} \frac{a^2}{r^4} \left( \frac{h^2}{5} - \frac{z^2}{3} \right) \right], \quad (4.13)$$

$$\widehat{rz} = - \frac{2kE(h^2 - z^2)}{3+\sigma} \frac{a^2}{r^2} \cos 2\theta, \quad (4.14)$$

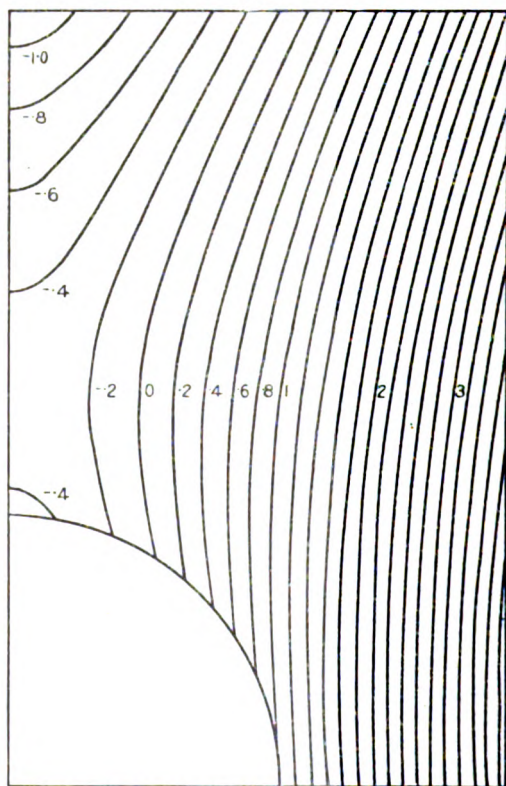
$$\widehat{\theta z} = - \frac{2kE(h^2 - z^2)}{3+\sigma} \frac{a^2}{r^2} \sin 2\theta. \quad (4.15)$$

These stresses do not vanish identically when  $r=a$ , *i. e.* at

the edge of the hole. In fact, the values there are :—

$$\begin{aligned}\widehat{rr}_e &= kEz \frac{6(2-\sigma)}{3+\sigma} \left( \frac{h^2}{5} - \frac{z^2}{3} \right) \frac{\cos 2\theta}{a^2}, \\ \widehat{\theta\theta}_e &= -kEz \left[ 1 - \frac{5-\sigma}{3+\sigma} \cos 2\theta \right. \\ &\quad \left. - \frac{6(2-\sigma)}{3+\sigma} \left( \frac{h^2}{5} - \frac{z^2}{3} \right) \frac{\cos 2\theta}{a^2} \right],\end{aligned}$$

Fig. 3.



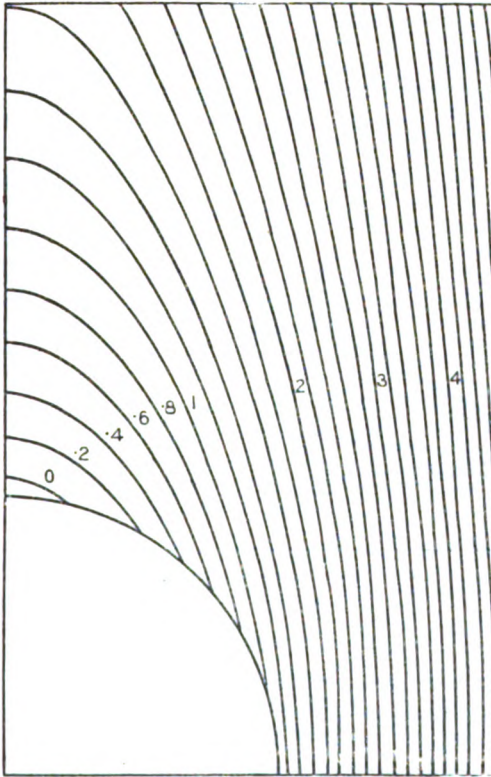
Contours near a hole in a plate bent anticlastically.

$$\begin{aligned}\widehat{r\theta}_e &= kEz \sin 2\theta \left[ \frac{2}{3+\sigma} + \frac{6(2-\sigma)}{3+\sigma} \left( \frac{h^2}{5} - \frac{z^2}{3} \right) \frac{1}{a^2} \right], \\ \widehat{rz}_e &= -\frac{2kE(h^2-z^2)}{3+\sigma} \frac{\cos 2\theta}{a} \\ \widehat{\theta z}_e &= -\frac{2kE(h^2-z^2)}{3+\sigma} \frac{\sin 2\theta}{a}\end{aligned}$$

From an examination of these formulæ, the general effect of the hole can be obtained, and also the limitations of the solution which are, of course, due to the simplifying assumption of a state of "generalized plane stress."

$\widehat{rr}$  is seen to be of the order  $h^2/a^2$ , compared with the stress in the absence of the hole. In fact, its greatest value, which occurs on the boundary of the hole where  $\theta=0$ ,

Fig. 4.



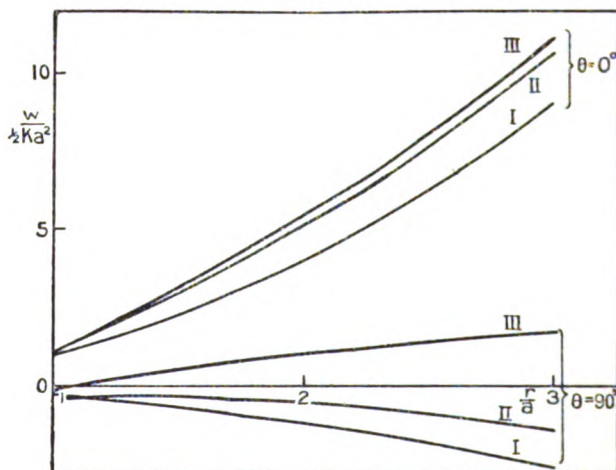
Contours near a hole in a plate bent into a cylinder.

and on the surface, is  $0.308 h^2/a^2$  times this. ( $\sigma=0.28$ , as before.)

$\widehat{\theta\theta}$  is comparatively large when  $\theta = \pm 90^\circ$ . There, neglecting the  $h^2$  term, its value is  $-8kEz/(3+\sigma)$ , *i. e.* more than twice (2.44 times, if  $\sigma=0.28$ ) the stress in the absence of the hole. For a plate of finite width this value would probably be modified, but it is certain that the maximum

stress would still be much greater at the edge of the hole than that calculated upon the assumption of a uniform distribution along the radius perpendicular to the straight edges. In fig. 6 the values of  $\hat{\theta}\theta_e$  for values of  $z/h$  are plotted (I.) without taking into account the hole, (II.) neglecting  $h/a$ , and (III.) for  $h/a = \frac{1}{2}$ , i. e. radius of hole equal to thickness of plate. The effect of the  $h^2$  term is seen to be very small. In fig. 7 the maximum stresses along the axes, neglecting the  $h^2$  term, are given as fractions of the maximum stress,  $kEh$ , in the absence of the hole.

Fig. 5.



Displacements of the central surface of bent plates containing a circular hole.

## 5.

It remains to devote a small space to the consideration of the residual stresses at the edge of the hole, and to show that they form a system of zero resultant, to which St. Venant's Principle may therefore be applied. Consider the resultant tractions on an element  $\delta\theta$  of the boundary. It is easy to verify that:—

$$\int r \hat{r}_e . dz = 0, \text{ i. e. there is no resultant radial traction.}$$

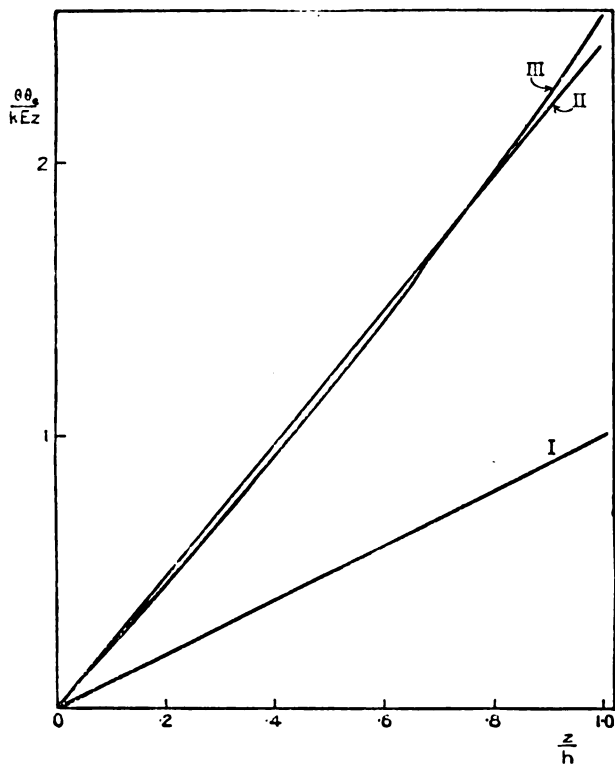
$$\int r \hat{r}_e . z . dz = 0, \text{ i. e. there is no bending couple about a tangent to the circumference.}$$

$$\int -r \hat{\theta}_e . dz = 0, \text{ i. e. there is no resultant tangential traction.}$$

$\int -r\widehat{\theta}_e . z . dz = -2Dkh(1-\sigma^2) \sin 2\theta/(3+\sigma)$ . This is a torsional couple, of amount  $H = -2Dkh(1-\sigma^2) \sin 2\theta/(3+\sigma)$  per unit length.

$\int r\widehat{z}_e . dz = -4Dkh(1-\sigma^2) \cos 2\theta/(3+\sigma)a$ . This is a resultant shearing force per unit length. Now the torsional

Fig. 6.



Stress  $\theta\theta_e$  at  $90^\circ$ .

couple  $H$  can be considered as applied \* by a distribution of shearing force

$$N' = -dH/a . d\theta = +4Dkh(1-\sigma^2) \cos 2\theta/(3+\sigma)a$$

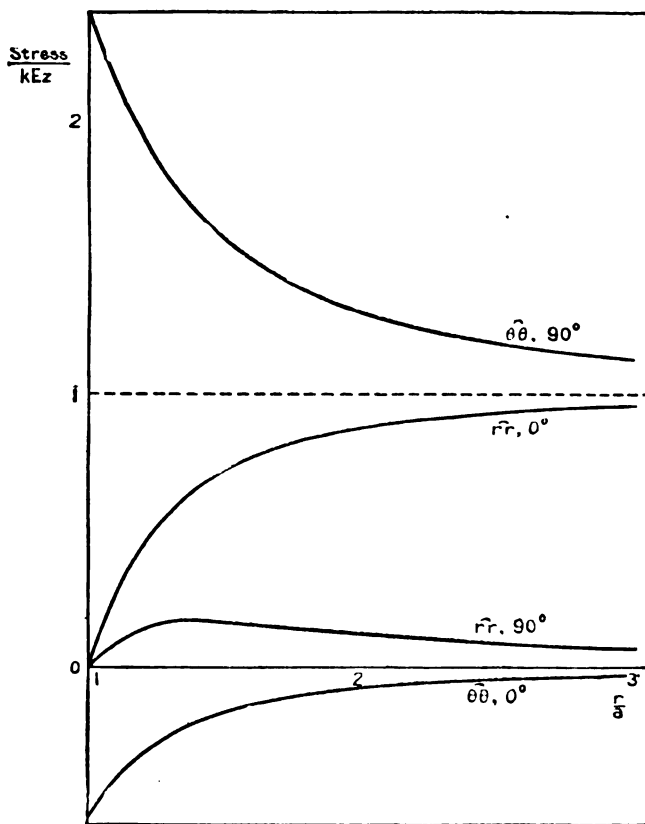
per unit length. This exactly neutralizes  $N$ . We thus see that the residual tractions form a system in equilibrium for any small element  $\delta\theta$  of the boundary, and consequently their effect is negligible at a small distance from the edge.

\* See, for instance, Love, *loc. cit.* p. 466.



A further investigation, eliminating these residuals, might be interesting mathematically, but would be of little practical importance.

Fig. 7.



Maximum stresses along the axes.

A similar detailed treatment of the plate bent into a cylinder would lead to similar results, but we content ourselves with the contours and displacements along the axes, already given.

London,  
February 1924.

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AND  
JOURNAL OF SCIENCE.

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[SIXTH SERIES.]

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DECEMBER 1924.

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XCVIII. *Why Wireless Electric Rays can bend round the Earth.* By Sir JOSEPH LARMOR, F.R.S.\*

THE earliest announcement that electric signals through free aether had been successfully detected as far as America by the Marconi operators, gave rise to a prompt query from the late Lord Rayleigh as to how the rays could manage to bend round the protuberance of the curved earth. In fact, in a single medium propagating waves without absorption or dispersion, all features remain similar when the scales of space and time are altered in the same ratio: thus waves of length  $\lambda$  bending round the earth of radius  $a$  will behave similarly to waves of length  $k\lambda$  bending round a smaller sphere of like quality of radius  $ka$ . To change from electric waves  $10^4$  cm. long to waves of light  $10^{-4}$  cm. long,  $k$  would be  $10^{-8}$ ; hence the radius of the sphere corresponding to the earth would be  $10^{-8} \cdot 10^{9\frac{1}{2}}\pi$  or 6 cm.; and familiar experience indicates that visible light could hardly creep to a sensible degree round one-tenth of the circumference of a sphere of that radius. To elucidate this subject quantitatively in those early days involved difficult and extensive calculations of the problem of diffraction of waves by a boundary, conducting or dielectric, of continuous curvature; and investigations by Lord Rayleigh, H. M. Macdonald, A. E. H. Love, J. W. Nicholson,

\* Read at the Cambridge Philosophical Society, Oct. 27. Communicated by Sir Oliver Lodge.

G. N. Watson and others have widely extended that domain of mathematical optics.

But nowadays, when ray-signals are readily received at the antipodes, all shadow of uncertainty as to the facts is removed. The rays could not travel free, except in straight lines, in a medium of practically uniform speed of propagation such as ordinary air; either they must be guided by being linked to the surface of the earth, much as cylindrical Hertzian waves follow a guiding central wire, or else the speed of propagation must for some cause increase notably upwards so as to bend them down. Very early observations by Admiral (then Captain) Jackson with the help of British cruising squadrons, showed that the high table-land of Spain was not an effective obstacle, which perhaps already pointed to transmission of the rays high in the atmosphere.

The ultra-rarefied upper atmosphere with its long free path must be subject to strong ionization by the incident ultra-violet solar radiation, the effect persisting after daytime, and appeal has been generally made to such a conducting layer to provide the necessary increase of velocity of the rays. But ordinary electric conduction operates by introducing a frictional term causing absorption into the equations, and it is a familiar principle that when the absorption is of the first order the change of speed is only of the second order, so that if the latter change is to be adequate, the rays would be damped out immediately instead of being sensibly transmitted. In rough illustration, the usual type (including the optical) of equation of propagation with frictional resistance of modulus  $\kappa$

$$\frac{\partial^2 \phi}{\partial t^2} + \kappa \frac{\partial \phi}{\partial t} = c^2 \frac{\partial^2 \phi}{\partial x^2}$$

is satisfied by

$$\phi = Ae^{-imx} e^{int},$$

where  $n^2 - \kappa ni = m^2 c^2$ , so that, for a real period  $2\pi/n$ ,

$$mc = (n^2 - i\kappa n)^{\frac{1}{2}} = n \left( 1 - \frac{1}{2}i \frac{\kappa}{n} + \frac{1}{8} \frac{\kappa^2}{n^2} + \dots \right).$$

Thus, retaining real parts, we arrive at a simple wave-train of type

$$\phi = Ae^{-\frac{1}{2}\frac{\kappa}{c}x} \cos n \left\{ t - \left( 1 + \frac{1}{8} \frac{\kappa^2}{n^2} \right) \frac{x}{c} \right\}$$

with extinction modulus  $\frac{1}{2}\kappa/c$  and velocity of propagation

$$v=c\left(1+\frac{1}{8}\frac{\kappa^2}{n^2}\right)^{-1}, \text{ or say } c\left(1-\frac{1}{8}\frac{\kappa^2}{n^2}\right),$$

thus smaller than  $c$ , but only to the second order in  $\kappa$ .

(On the principle of ray-curvature as *infra*, a ray of assigned period will adapt itself to the curvature of the earth only when

$$\frac{1}{2}\pi 10^{-9} = \frac{d}{dh} \log v = -\frac{1}{8n^2} \frac{d}{dh} \kappa^2.$$

The attenuation would vary inversely as the wave-length. If the wave-length is one kilometre,  $2\pi/n = \lambda/c = \frac{1}{3} 10^{-5}$ : so that if the rays are thus adapted over a vertical breadth of only a thousand metres the modulus of attenuation  $\frac{1}{2}\kappa/c$  must increase downward across it, so that at the lower boundary it mounts to at least  $10^{-6}$ , which means decay of amplitude in ratio  $e^{-1}$  after travelling only ten kilometres.)

To produce sensible bending of the rays without extinction, all action by conductive or other dissipation must thus be excluded. It would not suffice to say that the conductance has to become perfect, for then no waves could travel: the influence must be of dielectric type. A theory satisfying this criterion was hammered out in class-lectures at Cambridge on electric waves last February, and has been, in fact, already expounded in answers in the Mathematical Tripos much as it is proposed here to present it. The attention now excited by long-range free electric transmission, the most wonderful sudden practical evolution since the telephone, may attract the interest of a wider audience.

A sufficient cause for the increase of velocity, without dissipation, for waves travelling horizontally is, in fact, afforded by the free oscillations of ions even sparsely distributed in the very high regions of the atmosphere; though lower down their energy would be dissipated by collisions with the atoms and the travelling waves would be gradually quenched. Current is transmitted without any frictional loss across the vacuum of an electric valve by the jet of free electrons. On the other hand, in conduction in a metal the electrons or light ions get up speed at very rapid rate under the electric field, but at the end of each short free path they render up by collision part of the energy so acquired to the obstructing atoms of the metal, and this dissipation of the energy of the field is the measure of the electric resistance. For electric fields alternating at one-tenth of the rate of the waves of visible light, this process

of conduction is, as Rubens showed, fully established at each instant in metal—a fact which leads to some information as to the lengths of the free paths \*. But for ions travelling in an intensely rarefied upper atmosphere the free path will be long, so that many alternations of the electric force of the field of radiation, even for long electric waves traversing the medium, may occur within the time of one ionic path. This involves that the travelling ions will in the main swing free under the influence of the waves and thus interact without dissipation of their energy, scattering by secondary radiation from the slowly oscillating ions being negligible : there will thus be an influence on the velocity of the waves without absorption. To suit the present explanation the change ought to be a substantial increase, notwithstanding the small number of the ions contributing to it in the ultra-rarefied upper atmosphere. And the reason is simple. The influence of an ion is measured (jointly with the time) by the mean value of the alternating velocity excited in it, and this for a given intensity of field is proportional to the period of the waves, so that for long electric waves the effect may be millions of times as great as for short waves of comparable energy—in fact, it involves the square of the wave-length. Waves of shorter length could travel in a lower layer without excessive absorption, where a greater number of ions may make up for their weaker oscillatory motion †.

In passing, one may note that the same principle will apply in general terms to the penetration of X-rays of high frequency across metals, especially of low atomic mass ; when the time over a free path amounts to several periods of the radiation, the absorption, which must be due mainly to free ions, will be much diminished and the radiation can penetrate

\* Cf. Phil. Mag. August 1907.

† The only theoretical discussion which the writer has been able to find is by Dr. W. H. Eccles (Proc. Roy. Soc. p. 86, June 1912). A "Heaviside layer" above, so sharply bounded and so intensely conducting as to reflect the rays without penetration, is assumed, combined with an ionization of the middle atmosphere which bends them, but "in forming the equations it has been implicitly assumed that the ions are so heavy that they acquire only small velocities and make very small excursions under the action of the waves." A viscous term is inserted in the equation of motion of an ion ; if that term is annulled the formulæ must agree in form with those justified here for light ions of very long free path. The treatment is mainly by rays, and contains full discussion of the relevant observational material of that date, especially as regards stray radiations.

The diffraction theory of G. N. Watson (Proc. Roy. Soc. 1918, more recently studied) seems to make it unlikely that the ground can take any part in the actual transmission.

deeply—to a limit imposed mainly by simple dispersal or scattering, so proportional to the density of the atomic electrons: the Rubens experiments on reflexion of ultra-red light indicate a like result.

On general grounds the transparency of air for long electric waves would be expected to be great as compared with light; on account of the slow period molecular scattering is practically absent, and the mirage effects of local irregularities are negligible unless their extent is comparable with the wave-length (*cf.* p. 1032 *infra*).

The remark presents itself to contrast the finite free swayings of electrons or light ions in the ultra-rarefied gas of the upper atmosphere, which augment the speed of the exciting waves, with the finite swayings under the alternating attraction of the grid of a stream of electrons across a triode valve, which are thus partially trapped systematically by the grid and so establish its relay action.

There must thus be a layer high almost beyond the sensible atmosphere, within the auroral domain, in which a sheaf of horizontal electric rays, provided they are long enough, will travel without loss by absorption or scattering, concentration in this stratum being due to the potent influence exerted on the velocity of long waves by the free ions of small inertia interacting with them. But we have to suppose that the energy transmitted in this high stratum is being shed down to sensible degree all along the path, for the signals to be everywhere received. Introducing optical imagery, we can contemplate a special component ray-sheaf connecting the transmitter to every receiver situated along the path of the beam; these rays all gather together into a sort of caustic curve or layer up aloft, and so long as they are in it the energy travels onward without loss except by sideways spreading.

The question arises whether there can be enough energy to be thus showered down to receivers all over the earth. By a known principle a receiver collects energy over a range of order  $\lambda^2$ ; thus the total energy put into the transmitting layer is reduced at the receiver in the order of magnitude  $\lambda^2/4\pi a^2$ , so that for a wave-length of a kilometre the amplitude of vibration is reduced to the order  $10^{-4}$ , which is not excessive.

*Propagation of Long Electric Waves in Ionized Highly Rarefied Gas.*—One notes in the first place that the *aurora borealis*, due somehow to free ions, is displayed at a height of the order of fifty miles; this is ten times the height of

the homogeneous atmosphere, so putting aside effects of smaller order arising from change of temperature, the mean free path of the atoms would at that height be  $e^{10}$  times the value at the earth's surface, thus of the order of several centimetres. The number of molecules per cubic cm. would be  $3.10^{19}e^{-10}$ , or say  $10^{15}$ .

Let us then consider the motion of an ion of charge  $e$  and mass  $m$ , with free oscillation superposed on its translatory motion, due to the alternating electric field of radiation passing over it expressed locally by an electric force

$$F = A \cos pt, \quad 2\pi/p = \lambda/c.$$

For the oscillation thus superposed, all quantities being in electrodynamic units,

$$m\ddot{x} = eA \cos pt, \quad m\dot{x} = ep^{-1}A \sin pt,$$

so that the amplitude is  $ep^{-2}A/m$ . There are, say,  $N_0$  effective similar ions per unit volume, each supplying its contribution  $e\dot{x}$  to the electric flux; all ions, positive and negative, contribute in the same direction, but massive ones may be neglected. An electric current is thus produced of density  $C$  expressed in terms of the field  $F$  as

$$C = -N_0 \frac{e^2}{mp^2} \frac{dF}{dt}.$$

This current, of precisely the same type, adds, in the electrodynamic circuital equations of the exciting wave-train, to the usual Maxwellian dielectric "total current" of density  $\frac{K}{4\pi c^2} \frac{dF}{dt}$ , in which  $K$  is the static dielectric modulus of the medium and is practically unity for ordinary air. On adding them it comes out that the effective  $K$  is diminished to

$$K' = K - N_0 \frac{4\pi e^2}{mp^2}.$$

If  $c'$  is the velocity of propagation,  $c'^{-2}$  is thereby altered from the value  $K/c^2$ , or say  $c^{-2}$  in the absence of ionization, to  $K'/c^2$ ; so that

$$c'^{-2} \cong c^{-2} \left( 1 - N_0 \frac{e^2 \lambda^2}{\pi m} \right).$$

This increase of speed from  $c$  to  $c'$  arising from free ions mounts with  $\lambda$ , so for long electric waves it would be sensible, notwithstanding extreme tenuity of the gaseous ions. It would usually be of no account except in metals for the short waves of light.

Roughly the ionic charge  $e$  is of order  $\frac{3}{2}10^{-20}$  electro-magnetic; taking a wave-length of one kilometre,  $\lambda$  is  $10^5$ ; and if the effective ions are electrons  $e/m$  is  $\frac{7}{4}10^7$ ; the multiplier of  $c^{-2}$  on the right then becomes  $1-10^{-3}N_0$ .

What we are concerned for is that the rays should have a curvature exactly equal to that of the earth. The index of refraction is  $\mu = \frac{c}{c'} = 1 - N_0 \frac{e^2 \lambda^2}{2\pi m}$ , or, say here,  $1 - \frac{1}{2}10^{-3}N_0$ . So the curvature of the rays, which is  $-d\mu/dh$  (as *infra*) or  $\frac{1}{2}10^{-3} \frac{dN_0}{dh}$ , is not to fall short of  $\frac{1}{2}\pi 10^{-9}$ . For the present assumed data this condition of curvature requires  $\frac{dN_0}{dh}$  to be about  $3 \cdot 10^{-6}$ , a value which must extend over the effective layer, which may be a considerable range of  $h$ , say  $10^5$  cm.; and this mounts up for the terminal value of  $N_0$  to only about  $\cdot 3$  electrons or  $5 \cdot 10^2$  hydrogen ions per cubic cm., whereas at the height of 50 miles there are still  $10^{15}$  molecules of gas per cubic cm.

*Bending of Optical Rays.*—The directions of the wave-fronts are transverse to the rays, and consecutive rays meet at their centre of curvature: thus, considering as usual two adjacent rays of the coherent beam, at distance  $\delta n$ , as the time of transit is the same for both from one front to the next, and the element of path of the ray is  $v\delta t$ , we have  $\delta v/v = \delta n/R$ , so that the curvature  $R^{-1}$  of the ray is  $d \log v/dn$ , or here simply  $-d\mu/dn$ . Ordinary atmospheric refraction by the action of the molecules, according to this formula, as applicable to horizontal rays of light or electric rays, would be negligible at the heights here in question of the order of fifty miles; but at sea-level, where it is mainly due to temperature gradient, it would give a very substantial though insufficient contribution to the required amount of bending. For the refractive index of air for ordinary light, and also for long waves, is at sea-level 1.0003; and the curvature of a horizontal ray is  $-\frac{d\mu}{dh}$ , which as  $\mu - 1 \propto \rho$  is  $-3 \cdot 10^{-4} \frac{1}{\rho} \frac{d\rho}{dh}$ , if there is no gradient of temperature, or  $3 \cdot 10^{-4} \frac{g\rho}{p}$ ; wherein the speed of sound is  $\left(1.4 \frac{p}{\rho}\right)^{1/2} = 32400$  cm./sec. at  $0^\circ$  C., giving  $\frac{p}{\rho} = \frac{2}{3} \left(\frac{13}{4}\right)^2 10^8$ ; so that  $-\frac{d\mu}{dh}$  is  $3 \cdot 10^{-4} / \frac{2}{3} 10^9 \cdot 10^{-3}$  or  $5 \cdot 10^{-10}$ , which as the earth's radius is  $\frac{2}{\pi} 10^9$  amounts to as much as one-quarter of the



curvature of the earth. But actually the gradient of temperature  $d\theta/dh$  affects this result by a factor  $1 + 30d\theta/dh$  if  $h$  is measured in metres, and is the chief cause of mirage effects: for instance, the curvature of the ray would agree with that of the earth if the temperature increased upward by  $1^\circ\text{C}$ . for 9 metres\*. These temperature variations of the ordinary index of refraction in the lower atmosphere would likewise affect long electric waves, were it not for the saving limitation that irregularities occupying only a small part of a wave-length would be of no account; while at a height say of 15 kilometres, where the density of the air is reduced seven times, the effect is in any case very slight. As already remarked, the effective stratum is too high for meteorological instabilities to affect it. But it will not, of course, be exactly horizontal: its height may be expected to be some function of the local solar time at the place.

*Amplitude of Oscillations of Free Ions.*—We have still to verify that the amplitude and time of the oscillation of an ion would not be too great, in comparison with its free path, to allow a large degree of freedom in its vibrations.

The value of the amplitude is  $\frac{e}{mp^2}A$ , or  $\frac{e\lambda^2}{4\pi^2mc^2}A$ , where  $A$  is the amplitude of vibration of the electric force in the waves. If this field of force is  $V$  volts per cm. (which compares with ten volts per cm. for the field of full sunlight if it were coherent†) so that  $A=10^8V$ , the amplitude for an electron, with wave-length  $10^5$  cm. or one kilometre as above, is about  $\frac{1}{2}10^3V$ . It increases as the square of the wave-length. For a hydrogen ion it would be 1700 times smaller. Actually  $V$  is so small that even for an electron it fits amply within the gaseous free path at a height of fifty miles, where it is several cm. as above. But sufficient time

\* Cf. Everett's exposition of James Thomson's theory. *Phil. Mag.* p. 169, Mar. 1873: or Rayleigh, 'Theory of Sound,' ii. § 288.

† Maxwell (Treatise, § 793) seems to have miscalculated the results. Solar radiation is 2 cal./min. where 1 cal. =  $4.18 \times 10^7$  ergs: for this intensity, if the radiation were coherent, the amplitude of its electric field would be as high as 10 volts/cm., and of its magnetic field .034 or  $\frac{1}{3}$  of the mean horizontal force in Britain. The pressure of the solar radiation is 500 grammes weight per square kilometre. But the solar natural radiation differs from the artificial radiations here discussed (which hardly occur at all in nature) in being a statistical aggregation from molecular origins and not one coherent undulation: for it, energy is the surviving fundamental datum, definite amplitudes of oscillation must be replaced by deviations from a steady average state of disturbance measured by a statistical mean square, and theory would be of entirely different form—that of natural radiation.

as well as space must be provided for this postulated regular forced oscillation of the ions. The period of a wave-length of one km. is  $\frac{1}{3}10^{-5}$  sec.: the time for a molecular free path of 3 cm. would be of order rather more than 2 cm. divided by velocity of sound in the gas, which is, say, twenty times longer. But this is for air; for a hydrogen ion the time would be divided by at least 5, for an electron in thermal equilibrium perhaps by 200, unless its path were lengthened by passage through the atoms without much disturbance of its motion. Thus it is only in the ultra-rarefied upper atmosphere that the slow alternations of material ions under the influence of long electric waves would have time or space for many complete oscillations on one free path; and there Ohm's law would be wholly inapplicable.

If there are  $N_0$  ions per cubic cm., each  $M$  times the mass of an electron, and the time in the free path is  $n$  times the period of the waves, of electric amplitude  $F_0$ , then in one second energy  $\frac{F_0^2}{8\pi c^2}c$  passes across one sq. cm., while within

one cubic cm. energy  $\frac{N_0}{n} \frac{e^2 \lambda^2}{8\pi^2 m c^2} F_0^2 \frac{1}{c}$  is dissipated in one second: by dividing, the modulus of absorption per cm.

comes out  $\frac{N_0 \lambda}{n M} 10^{-13}$ . In the circumstances illustrated above  $n$  may be 10,  $N_0$  is  $2 \cdot 10^3$  hydrogen ions for which  $M$  is 1740, the wave-length  $\lambda$  is  $10^5$  cm., so that plane radiation would be reduced by ionic absorption acting alone in ratio  $e^{-1}$  in a path of ten thousand kilometres. This compares with the estimate given earlier of the effect of conductance.

We infer that the present type of explanation by a velocity of propagation increasing with height, which bends down the rays without undue absorption, is sound and reasonable for electric waves of the lengths usually employed, if only a very small proportion of the molecules of the upper air were ionized, so as to provide electrons or light ions, by the intense ultra-violet solar radiation. Across the region of the dawn the strata of ionization may be deranged: they may be deformed locally so much as to throw the concentrated horizontal sheaf of rays upward into space or else downwards to the earth so far that it cannot recover the horizontal direction in the new effective stratum. But if that stratum is deep, say a kilometre, such dislocation need not be complete. These considerations retain general validity when the strata of equal ionization are not exactly horizontal.

There seems to be some call here for closer scrutiny of

statistics as to the relation of range to wave-length : also as to whether reception is better or worse, or simply irregular, at times of dawn or sunset \*. It is perhaps significant that "atmospherics" are reported to predominate at sunrise and sunset. It appears also † that there is increase of strength but diminished direction-finding at night : that in both respects North-South is superior to East-West : that winter is favourable in the Atlantic, and transmission over sea easier than over land.

Scrutiny of the induced electric moment of a molecule in a strong field is here incidentally suggested. For air at standard density the refractive index is of order  $1 + 3 \cdot 10^{-4}$  : thus the induced polarity  $\frac{K-1}{4\pi} F$  in electrostatic measure is  $\frac{1}{2} 10^{-4} F$  distributed over  $\frac{3}{2} 10^{19}$  molecules. If  $F$  is  $\frac{1}{2} 10^5$  volts per cm. (corresponding to a spark of 5 cm.), which is 60 electrostatic units, this gives a moment  $2 \cdot 10^{-22}$  for each molecule. As  $e$  is  $5 \cdot 10^{-10}$  electrostatic, the arm of the moment would be  $4 \cdot 10^{-13}$  cm., while the molecular radius is as much as  $10^{-8}$ . Thus  $K$  would hardly fall away from being constant before the field approached  $10^6$  electrostatic, and disruption would have set in long before.

*Undulatory Propagation for a Thin Unchanging Sheaf of Rays.*—The electric radiation to great distances thus involves a sheaf of rays whose breadth may be only a fraction of one of its long wave-lengths, which travels along a surface of constant index, while it has to remain concentrated without spreading either by refraction or by diffraction. The subject thus invites examination dynamically. The equation of propagation, neglecting now the terrestrial curvature of the strata, is of type

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} = c'^{-2} \mu^2 \frac{\partial^2 \phi}{\partial t^2}, \quad \mu^2 = 1 + \psi(z),$$

where  $c'$  is the speed along the mid-front at which  $\psi(z)$  vanishes. The type of waves here contemplated, with amplitude changing along the front as  $f(z)$ , is expressed by

$$\phi = f(z) F(x - c't);$$

\* It appears (Eccles, *loc. cit.* p. 97) that in transatlantic signalling the response, in fact, does attain a high maximum when either the receiver or the transmitter is in the dawn or the sunset : and other significant features are found.

† Cf. Prof. E. V. Appleton, Royal Institution Lecture, in 'Engineering,' May 30, p. 709.

but this must be further specialized for the analysis, into harmonic trains each of type

$$\phi = f(z) \cos m(x - c't), \quad m = 2\pi/\lambda.$$

Then 
$$\frac{\partial^2 f}{\partial z^2} - m^2 f = -m^2 \{1 + \psi(z)\} f,$$

or 
$$\frac{\partial^2 f}{\partial z^2} = -m^2 \psi(z) f, \quad \mu^2 = 1 + \psi(z).$$

For a disturbance with its parts keeping together as it travels,  $f(z)$  must fall off on both sides of a maximum along  $z=0$ : that is, the graph of  $f(z)$  must be concave to the axis of  $z$ , the condition for which is  $\partial^2 f / \partial z^2$  negative; so that as the amplitude  $f$  is positive,  $\psi(z)$  must be positive on both sides of the central plane. This is simply the familiar condition that the stratum is to be one of minimal index, close to which the rays must cling by virtue of the principle of minimal time of transit.

Over small range of  $z$  we may illustrate by taking

$$\mu = 1 + \Lambda z^2:$$

the equation to determine the law of transverse intensity for such an unchanging layer of the wave-train is

$$\frac{\partial^2 f}{\partial z^2} + 2m^2 \Lambda z^2 f = 0,$$

which is amenable to simple graphical treatment.

The actual effective atmospheric stratum must, however, be curved to the earth's radius  $a$ , and the equation of wave-propagation of the curved sheaf of rays travelling along it is of type

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \phi}{\partial \theta^2} = c_0^{-2} \mu^2 \frac{\partial^2 \phi}{\partial t^2}, \quad r = a + z,$$

where  $c_0$  is the velocity along  $z=0$  and  $\mu$  is the index relative to that layer.

The type of waves travelling along it without spreading may as before be restricted to the harmonic form

$$\phi = f(z) \cos m(a\theta - c_0 t), \quad m = 2\pi/\lambda.$$

As  $r = a + z$  this gives

$$\frac{\partial^2 f}{\partial z^2} + \frac{1}{a+z} \frac{\partial f}{\partial z} - \frac{m^2 a^2}{(a+z)^2} f + m^2 \mu^2 f = 0.$$

Thus if

$$g = (a+z)^{\frac{1}{2}} f, \quad \mu^2 = 1 + \psi(z),$$

$$\frac{\partial^2 g}{\partial z^2} + \left\{ \left( \frac{1}{4a^2 m^2} - 1 \right) \left( 1 + \frac{z}{a} \right)^{-2} + 1 + \psi(z) \right\} m^2 g = 0.$$

As before, the layer of transmission extends over the values of  $z$  which make the coefficient of  $g$  in this equation positive; for  $z$  small it approximates to

$$m^2 \left( \mu^2 - 1 + \frac{2z}{a} - \frac{3z^2}{a^2} + \frac{1}{16\pi^2} \frac{\lambda^2}{a^2} \right).$$

Thus substituting

$$\mu = \mu_0 + \left( \frac{\partial \mu}{\partial z} \right)_0 z + \frac{1}{2} \left( \frac{\partial^2 \mu}{\partial z^2} \right)_0 z^2 + \dots,$$

this equation in  $g$  takes the same form as the previous one in  $f$ , found as the analytical expression of the concentration of the rays for flat strata towards the straight ray of absolutely least time of transit, provided that when  $z=0$

the curvature  $a^{-1}$  is equal to  $-\left( \frac{d\mu}{dz} \right)_0$ , as before obtained, and also  $\mu_0 \left( \frac{\partial^2 \mu}{\partial z^2} \right)_0 - \frac{2}{a^2}$  is positive.

It may be remarked that treatment of the cognate subject of optical mirage involves a like analysis\*.

XCIX. *On Sommerfeld's and Landé's Rules for Classification of Terms and Zeeman Patterns in Spectra.* By W. M. HICKS, F.R.S., Emeritus Professor of Physics, Sheffield †.

WITHOUT doubt one of the most important advances in the analysis of spectra since Rydberg's discovery of the combination law is the recent extension‡ of Sommerfeld's system of enumeration of species of term-types by Landé, combined with the completion of the latter's rules for predetermination of Zeeman patterns by the discovery of a formula for the splitting factor  $g$ , and the experimental establishment§ of these rules by Back, and by Gieseler. The present communication contains I. a suggested change in form of the enumeration and the rules, and II. a discussion of the evidence for and against a rule, accepted by Landé, supposed to give the ratios of the separations in multiplets.

\* Cf. Everett, *loc. cit.*

† Communicated by the Author.

‡ Sommerfeld, *Ann. d. Physik*, lxx. p. 32 (1923); Landé, *Zeits. f. Phys.* xv. p. 189 (1923).

§ Back, *Zeits. f. Phys.* xv. p. 206 (1923); Gieseler, *Ann. d. Phys.* lxxix. p. 147 (1922).

## I.

In order to bring out the essential nature of this method of classification I begin by recalling, in a quasi-historical order, the evidence by which the present enumeration has been arrived at. In doing this I assume the reader to be already acquainted with the classification itself.

It was early recognized that the observed series depended almost wholly on combinations of—or transitions between—selected sequences. In fact only combinations  $sp, pd, df, \dots$  or, in other words, if written in order  $s, p, d, f$  transitions only take place between neighbouring letters. This may be regarded as a true statement of normal conditions, if by “normal” is understood those transitions which take place most frequently. Transitions between terms of the same sequence are also common in certain types, e.g.,  $p, p$  and  $d, d^*$ . But transitions  $s, d \uparrow$  or  $p, f$  are rare, and seem to require a more severe excitation and in some cases the presence of an electric or magnetic field.

When Sommerfeld gave his extended theory of quantization of the generalized coordinates of a system, and applied it to a special model of a single electron circulating round a sheathed nucleus, he deduced, as is well known, the term-formula  $N/\{m + \mu + \alpha/(m + \mu)^2\}^2$ , in which  $m$  is the sum of the radial and azimuthal numbers and  $\mu, \alpha$  are functions of the azimuthal alone. It was natural therefore at once to draw the inference that the different types were determined by their azimuthal quanta. The possibility of a zero value of  $m$  was excluded as it was supposed that an electron oscillating in a line through the nucleus was impossible. Hence a zero azimuthal number is also excluded. Consequently  $s, p, d, f$  or succeeding  $g, h, \dots$  were supposed to

\*  $pl - pm$  sets are so common in arc spectra as to be expected when searching a spectrum for P series, for which they are used to establish doubtful P allocations, or to extend the series beyond observed regions. All multiplets whose lines show a common  $Z.P = 0.3.2 - L$  category of my ‘Analysis’—are due to transitions between terms of the same type, and they occur as strong sets not only in all the spectra of the alkaline earths, but in many others (Popow) whose series relations are not yet fully established. Similarly  $d, d$  multiplets occur in all the alkaline earths. As striking instances may be adduced a  $dd$  multiplet in Mn and  $0.3.2$  multiplet in Cr. Their lines occur in the lowest temperature furnace spectra of King.

† Messrs. Foote, Mohler, and Meggers (Phil. Mag. xliii. p. 459) find strong lines  $s1 - d2$  in Na and K in cases where electric or magnetic fields are excluded, also seen by Datta (Proc. Roy. Soc. 101. p. 545) as absorption lines. But although showing that the exclusion of such transitions is not absolute, they do not affect the general statement that such are rare, i.e. abnormal in the sense above.

depend on successive azimuthal numbers 1, 2, 3 .... Thus a term-type is definitely fixed by an expression  $n_k$ . We need not stop to consider difficulties in connexion with assignation of azimuthal quanta to term-type, as that is outside our present subject, but if we decide to enumerate types by successive numbers, these numbers 1, 2, ... are the simplest. In this case the observational facts referred to above give the normal transitions by

$k \rightarrow k-1$ , or  $k+1$  and  $k \rightarrow k$  (restricted cases). Rule I.

Bohr deduces from his principle of correspondence that  $k \rightarrow k$  is impossible if  $k$  is an azimuthal number. The experimental facts indicated above would seem to require some modification either in the principle of correspondence or in the azimuthal quality of the  $k$ .

The next step is to classify the satellite effect, which shows the existence of more than one species in a type. Thus in doublets there are one  $s$ , two  $p, d, f$ , and in triplets one  $s$ , three  $p, d, f$ —at least in elements of group II. Sommerfeld co-ordinates these by a new set of successive integers\*—now written  $j$ —an individual term being now represented by  $n_{ki}$ . Here the experimental fact ruling conditions is that we never find transitions from more than three species of one type to one of another (see, however, Note at end). In other words, in the arrangement of any multiplet in regular order the lines appear in sets of three only. Thus, if we decide to use successive integers in classifying species of types, we get Sommerfeld's transition rule

$j \rightarrow j+1, j, j-1$ . . . . Rule II.

We might equally well decide to use say successive even numbers, when the rule would be  $j \rightarrow j+2, j, j-2$ , or any other regular succession. The important fact now emerges, that after settling this successive order, all the  $j$  of all the types depend uniquely on the value chosen for one, say the singlet or doublet  $s$ , which is a type of only one species. It will be sufficient here to indicate how this results without going into actual details. Consider first the case of elements which have an even number of external or removable electrons and which produce singlets, triplets—(Rydberg's rule).—In the singlet all the terms are single. We decide (*i.e.* Sommerfeld) to give  $j = 0$  to  $s'$ . We find a relation

\* The attempts of Sommerfeld and his associates to explain these numbers by picture models are another matter, and, however useful and suggestive, tend to obscure their experimental origin. We shall refer to them as  $j$  values instead of internal quanta, thus leaving their real origin an open question, as indeed it is.

between singlets and triplets by the  $s'-p_2'''$  lines, with no  $s'-p_1'''$  and with  $s'-p_3'''$  weak or requiring excitation by the spark, *i. e.* not normally radiated. It is necessary then, if rule II. holds, that the  $j$  for  $p_{1,2,3}$ \* should run 2, 1, 0. This excludes the combination  $s'p_3'''$  but allows the others. To meet the exclusion of  $s'p_3'''$  Landé has added an additional rule

$$j = 0 \rightarrow j = 0 \text{ forbidden, } \dots \text{ II}_a.$$

and it is suggestive that in the new manifolds recently discovered the corresponding two lines—e. g.  $s'-p_{2,3}'$ , where no  $j = 0$  can be in question, both exist as strong lines in the arc. The rule is justified also as it is required to reproduce the observed combinations in the L—or 0/3/2—multiplets in which  $p_3-p_3$  (*i. e.*  $j = 0$  to  $j = 0$ ) is not observed. With  $p'''$  settled as 2.1.0, the D sets necessitate 3.2.1 for  $d_1, d_2, d_3$  and the F 4, 3, 2 for  $f_1, f_2, f_3$ , in order that rule II. may exclude  $p_2 d_1, p_2 d_1, p_3 d_2$  and allow the others, etc.

It will be noticed that where  $p$  is single so are  $d, f$ , when  $p$  is double so are  $d, f$ , and when  $p$  is triple so are  $d, f$ . This fact led Sommerfeld to formulate a statement which he called the “permanency of multiplicity,” which represented facts as known at the time. But in the spectrum of Mn and Cr Catalan in 1922 found series in which  $s$  was single,  $p$  triple, and  $d$  fivefold. These discoveries revolutionized ideas in spectral classification and at the hands of Landé have given us for the first time definite tests of term character, and the power of predetermining Zeeman patterns.

Catalan's discovery—at once extended by other investigators—showed that we must add yet another category of spectral terms, and that groups of  $s.p.d \dots$  exist other than those of singlet, doublet, and triplet groups. Landé gave precision to Sommerfeld's “permanency of multiplicity” by referring the statements to the particular multiple group. The multiplicity of the terms increases by two successively up to a permanent value determined by the attainment of a  $j$  value = 0. Thus in the quintet system  $s$  is single,  $p$  triple,  $d$  fivefold (here  $j = 0$  for  $d_3$ ) with  $f$  and all terms beyond fivefold. Thus each group can be classed according to its permanent multiplicity. Landé denotes this by  $r$ —the term by  $n_{kj}$ , say  $n(k, j, r)$ —and again attached a name, Rumpfquantumzahl, which depended on a picture model which may possibly be discarded with further knowledge. I shall refer

\* We keep the old numeration where  $p_1$  is the term which gives the most intense line and which corresponds to the highest energy level, or lowest energy value.



to it as its  $r$  class, and propose to denote the group as a manifold \*. Thus a fivefold group contains  $s$  with singlet,  $p$  with triplet,  $d.f.g$  ... with quintic multiplicities. The transition rule is

$$r \rightarrow r+2, r, r-2. \dots \text{Rule III.}$$

It may be noted that Landé's  $j$  classification is uniquely determined (subject to choice of  $j$  for  $s$  in the four and five folds) by observed data. Just as the relations between those of the one and three folds are related by the intercombinations  $s^1-p^3$ , so those of the five and seven folds, and those of the six and eight folds are connected by intercombinations of  $s^5-p^7_{2,3}$  in Cr and  $s^6-p^8_{2,3}$  in Mn. At present there are no observational data to relate the three and five folds, but Landé's classification meets this by choosing  $j$  for  $s^5$  by analogy. We may note that in group II. with two external electrons we have one- and three-fold groups, in group VI. (Cr, Mn<sup>+</sup>) with six, five- and seven-folds, in group VII. (Mn, O<sup>+</sup>) with seven, six- and eight-folds, in group I. with one, no- and two-folds. We are justified, therefore, in inferring at least provisionally that an atom—neutral or ionized—with  $n$  external electrons radiates in series depending on terms in  $n-1$  and  $n+1$  folds, and more copiously in the  $n-1$ . But that such a rule is not exclusive is shown by the fact that O exhibits a  $0/3/2$  multiplet of threefold type (see also Note at end).

Rule III. forbids a transition between even and odd manifolds, which accords with the well-known fact that in any one element such manifolds belong to different radiating atoms. The two systems for even and odd manifolds are therefore quite independent and may start from different initial  $j$  for the singlet  $s$ . The choice of 0 for  $s^1$  and 1 for  $s^2$  is therefore arbitrary, as well as the intervals between successive  $j$ . For instance it is open to us to take successive even numbers, starting from 0 for odd folds, and successive odd numbers starting from 1 for even folds. The transition rule II. would then be

$$j \rightarrow j+2, j, j-2. \dots \text{Rule II'}$$

In this way the oddness or evenness of  $j$  would refer to the oddness or evenness of the number of external electrons associated with the transition-electron. Further, with this numeration transitions between odd and even folds would also be forbidden by rule II'. This is not by itself sufficient inducement to change Sommerfeld and Landé's basis of

\* Permanent multiplicity is too long, and multiplicity by itself is needed to define that of a term type.

numeration, but the inducement is strengthened when the greatly increased simplicity in Landé's rules for the pre-determination of Zeeman patterns is considered. This is indicated by putting side by side the corresponding rules under the two systems. The  $j, g$  values for the two terms of a combination are represented by  $j_x, g_x$  and  $j_y, g_y$  with  $j_x \geq j_y$ . In each scheme the  $j$  and  $g$  are to be supposed expressed in their respective ways.

Old Scheme.	Equation for $g$ .	New Scheme.
1.	$\left. \begin{aligned} 3 + \frac{r^2 - (2k-1)^2}{8j(j+1)} & \text{ for odd folds} \\ 3 + \frac{r^2 - (2k-1)^2}{2(2j-1)(2j+1)} & \text{ for even} \end{aligned} \right\}$	$\frac{3}{4} + \frac{r^2 - (2k-1)^2}{4j(j+2)}$
2.	Rule for multiplying factor— $m$ in $mg$ .	
	$m = \text{successive integers from } j$ to $-j$ including 0 for odd folds $m$ less by $\frac{1}{2}$ excluding 0 for even	$m = \text{integers from } j \text{ to } -j$ intervals of 2
3.	Components follow one another at intervals $e =$	
	$g_x - g_y$	$2(g_x - g_y)$
4.	The spread between the strongest components. This depends on whether $j_x, j_y$ are different or equal.	
	$j_x, j_y$ different.	
$\pi$ .	0 for odd $g_x - g_y$ for even	0 for odd $2(g_x - g_y)$ for even
$\sigma$ .	$\left. \begin{aligned} 2(j_x g_x - j_y g_y) & \text{ odd} \\ (2j_x - 1)g_x - (2j_y - 1)g_y & \text{ even} \end{aligned} \right\}$	$2(j_x g_x - j_y g_y)$
	$j_x, j_y$ equal.	
$\pi$ .	$\left. \begin{aligned} 2(j_x \sim g_y) & \text{ odd} \\ (2j-1)(g_x \sim g_y) & \text{ even} \end{aligned} \right\}$	$2(j_x \sim g_y)$
$\sigma$ .	$\left. \begin{aligned} 2g_x \text{ and } 2g_y & \text{ odd} \\ g_x + g_y & \text{ even} \end{aligned} \right\}$	$\left. \begin{aligned} 4g_x \text{ and } 4g_y & \text{ odd} \\ 2(g_x + g_y) & \text{ even} \end{aligned} \right\}$
5.	Number of components.	
$\pi$ .	$\left. \begin{aligned} 2j_y + 1 & \text{ odd} \\ 2j_y & \text{ even} \end{aligned} \right\}$	$j_y + 1$
$\sigma$ .	$\left. \begin{aligned} 2(j_x + j_y) & \text{ odd} \\ 4j_y & \text{ even } (j_x > j_y) \\ 2(2j_y - 1) & \text{ even } (j_x = j_y) \end{aligned} \right\}$	$j_x + j_y$

The greater simplicity of the new arrangement is clear. Possibly also it may render it possible to dispense with half quanta in the picture model illustrating the classification. The establishment of Landé's rules for the Zeeman pattern by the experimental work of Back shows conclusively that the Sommerfeld-Landé's  $k, j, r$  method of enumeration corresponds in some way to an ordered arrangement within the atom. It is possible that additional sub-classes may be necessary with more complete knowledge. Such a necessity is suggested by observational data which appear to exhibit more than one  $n(k, j, r)$  term, but until an analysis of these new spectra has been made no definite conclusion can yet be drawn.

The statements as to the number of  $\omega$  and  $\sigma$  components require a limitation. They are true provided none of the calculated components coincide. This may happen in two ways:

(a)  $g_x = g_y$ . In this case all the  $\omega$  and all the  $\sigma$  coalesce to form a triplet with a  $\sigma$  shift of  $g$ . As an example is the L category of multiplets ( $r = 2k - 1$ ) in which the Z.P. reduces to the triplet  $0/3/2$ .

(b) This affects only the number of  $\sigma$  components. The magnitude of the shifts on one side of the original line may be regarded as given by all the arrows in a Landé diagram which slope in one direction, no regard being paid to sign. Using the new scheme of numeration the extreme shift is  $j_x g_x - (j_x - 2)g_y = 2g_x + (j_x - 2)(g_x - g_y)$ . All the shifts are then given by

$$2g_x + (j_x - 2)(g_x - g_y) - n \cdot 2(g_x - g_y),$$

where  $n$  ranges from 0 to  $\frac{1}{2}(j_x + j_y) - 1$ . Should any of these be numerically equal (opposite sign), the corresponding components in the pattern will coincide. The condition is therefore

$$2g_x + (j_x - 2 - 2n)(g_x - g_y) = -\{2g_x + (j_x - 2 - 2n')(g_x - g_y)\},$$

$$\text{whence } n + n' = j_x - 2 + \frac{2g_x}{g_x - g_y}.$$

Hence a necessary condition is that  $2g_x/(g_x - g_y)$  is integral  $= p$  say. But  $n + n'$  is necessarily less than the sum of the maxima of  $n, n'$ , i. e.  $n + n' < j_x + j_y - 2 > 0$ . Hence

$$j_x - 2 + p < j_x - 2 + j_y > 0,$$

$$2g_x/(g_x \sim g_y) < j_y;$$

or in Landé's system

$$2g_x/(g_x \sim g_y) < 2j_y \text{ for odd folds, } 2j_y - 1 \text{ for even.}$$

As an instance may be taken  $n_{4,4}^3 - n_{5,3}^3$ , or say in the old notation  $f_1''' - g_3'''$  \*. Here using Landé's numeration

$$j_x = 4, \quad g_x = \frac{5}{4}, \quad j_y = 3, \quad g_y = \frac{3}{4}, \quad p = 5 < 2j_y.$$

The Landé diagram is

$$\begin{array}{ccccccc} -\frac{20}{4} \dots\dots & -\frac{5}{4}, & 0, & \frac{5}{4}, & \frac{10}{4}, & \frac{15}{4}, & \frac{20}{4}, \\ & -\frac{9}{4} \dots & -\frac{3}{4}, & 0, & \frac{3}{4}, & \frac{6}{4}, & \frac{9}{4}, \end{array}$$

whence the Z. P. follows at once as

$$0.2.4.6/1.1.3.5.7.9.11/4,$$

with six side  $\sigma$  components instead of seven as given by the rule 5 above. There are many cases in which the first condition,  $p = \text{integral}$ , is satisfied, but in a few only are the  $j$  large enough to satisfy the second.

## II.

Landé enunciates a theorem relating to multiplet separations which appears as a deduction from the model. It is that the separations between the species of a term-type are proportional to  $\frac{1}{2}(j^2 - j'^2)$  in even folds or  $\frac{1}{2}(j - j')(j + j' + 1)$  in odd. In other words the successive separations are proportional to  $\frac{1}{2}(j + j') - (j = j' + 1)$ —for even and  $\frac{1}{2}(j + j' + 1)$  for odd (in new system  $\frac{1}{2}(j + j' + 2)$  for all folds). Consequently they run

$$3 : 5 : 7 : \text{ in even folds.}$$

$$1 : 2 : 3 : \text{ in odd } ,,$$

In support of this rule he has adduced some data which lead him to think that the statement is approximately true. If the rule is a true statement, its significance is so important that I propose to examine how far the data at our disposal support it, or the contrary. In treating the data the ratio of the separations will be given in terms of the smallest, treated as 1.

In the first place we should remember that the rule as stated cannot be true with absolute exactness, for these separations have their source in changes in the denominator of the Rydberg term-function, and it is to these displacements that any such rule would be applicable. Nevertheless, the changes in the ratios of the actual separations ( $\nu_1, \nu_2 \dots$ ) from those of the corresponding denominator displacements

\* Here  $g$  refers to term-type, not splitting factor.

( $\Delta_1, \Delta_2 \dots$ ) will be very small, unless the separations themselves are considerable\*. The effect is to diminish the rate at which the separations increase, below that of the real changes ( $\Delta \dots$ ), except where as in the almost unique case of Mn the displacements are of the opposite sign, when the rate is increased. In the present case, however, the observed separations are not so large as to produce an essential modification.

If a set of separations are in a ratio given by an arithmetic series, as here, the fact shows itself at once by the constant differences between them. This test is of course not applicable to triplets. We find a few cases only in the lately recognized multiplets, so that their fewness is rather *à priori* against the rule as applicable to multiplets with any closeness.

In considering the data we must also remember that throughout a series, the separations tend to keep the same ratio approximately for all orders. If therefore there is agreement with the rule for the first order, it is no additional evidence in favour if succeeding orders are also adduced, nor on the other hand is the evidence against increased by considering all the orders when the first is in disaccord. This consideration applies to the case of the F series in  $Al^+$ , adduced by Landé, in which close agreement is found for nine successive orders.

The question also will arise as to what is to be taken as approximate agreement. For instance, say theory requires a ratio  $3/2=1.5$  and observation gives 1.66. At first sight this might be taken as a rough agreement, but as a fact it corresponds to a ratio 5:3, and really contradicts a theoretical 3:2. It must be remembered that the observed ratios are definite up to at least the third decimal place. We should then estimate agreements as between numbers of three significant figures. Further, it is not legitimate to average two numbers deviating equally from those expected, as for instance Back † with an expected ratio 7:5 and two observed ratios 7:4.3 and 7:5.7. These are probably really cases of 4.33 and 5.67 corresponding to exact ratios 21:13 and 21:17.

With these preliminary remarks we proceed to the actual data, taking those of each manifold by themselves—the odd first. The two-folds or doublets do not of course enter.

\* *E.g.* in Hg,  $v_1 : v_2 = 4630.467 : 1767.279$  (R/A) = 2.620.  $\Delta_1 : \Delta_2 = 87819.08 : 30008.03 = 2.927$ .

† *Zeits. f. Phys.* xv. p. 223.

After each term symbol are given the  $j$  values and next the Landé ratio.

Three-folds.

$p^3, j=2.1.0$	$2:1=2$		
A 2.37	Be 3.57		Al <sup>+</sup> 2.08
Kr 2.31	Mg 2.03	Zn 2.045	O 2.52*
X 2.18	Ca 2.03	Cd 2.16	Se 2.32?
Ra Em 2.03	Sr 2.10	Eu 2.62	
	Ba 2.37	Hg 2.62	

\* from a triplet  $0/3/2$  multiplet (Paschen and Back, *Ann. d. Phys.* xxxix. p. 914). Its separations 195.83, 77.59 are much larger than those of the generally accepted OP, which is definitely a five-fold set. The generally accepted SeP, also with large seps: is also possibly a three-fold P, and if so comes in here.

$d^3, j=3.2.1$	$3:2=1.5$		
A ?	Mg ?	Zn 1.17	Al <sup>+</sup> 1.30
Kr 1.69	Ca 1.44	Cn 1.64	
X* 1.65; 1.66	Sr 1.68	Eu 1.66	
Ra Em* 1.68; 1.75	Ba 2.10; 1.65†	Hg 1/1.71 §	

\* two independent D sets. † a second incomplete D set—the accepted D is very irregular. § The well-known abnormality in Hg with inverse to normal ratio.

$f^3, j=4.3.2$	$4:3=1.33$		
Sr 1.43	Cd ?	Al <sup>+</sup> 1.32*	
Ba 1.2	Eu 1.77		
	Hg ?		

\* the largest  $f$  sep: it gives the best agreement with Landé.

Multiplets.

A. $dd, j=3.2.1$	$3:2=1.5$	B. $dp, j=2.1.0$	$2:1=2$
Ca 1.50		Ca 2.46	
Sr 1.51		Sr 3.18; 2.53	
Ba 1.52; 1.66*		Ba 4.07	

\* Error in 'Analysis,' p. 68. Should be 4.48.3 : 3.39.5 = 1.66.

L. $pp, j=2.1.0$	$2:1=2.$		
Be 1.50		Al <sup>+</sup> 1.92	
Mg* 2.1		O 1.89	
Ca 1.84, 1.94			
Sr 1.32†, 1.94			
Ba 1.753 t... 2.407			

\* Paschen and Götze give this as a  $0,3,2$  set, which must be very doubtful. The lines are portions of  $S_{1,2,3}$  (5) and ( $\Delta_2$ )  $S_{1,2,3}$  (5) ('Analysis,' p. 263). Their allocation gives a denominator 5.33 quite out of step with others of this type.

† The single line for  $p_2 - p_3$  in Sr given by Götze (*A. d. Phys.* lxvi. p. 291) is clearly anomalous. There appears some analogy with Ba which gives two mutually displaced lines, with a separation giving a possible ratio close to 1.9. See 'Analysis,' pp. 223, 224.

*Five-folds.*

$p^3, j=3.2.1$		$\star 3:2=1.5$	
O 1.81	1.71	Cr 1.567;	$p^a, 1.463; p^b, 1.18$
S 1.55	1.55	Mn <sup>+</sup> 1.571	
Se 2.32	1.30	Cl <sup>+</sup> 1.674	

\* Analogous triplets in O. S. Se.

$d^3, j=4.3.2.1.0$	$4:3:2:1$
Cr 3.538: 2.794: 1.943: 1	
Mn <sup>+</sup> 4.593: 3.195: 2.047: 1	

L or 0/3/2 multiplets, $dd'$ in Cr	
1.702: 1.513: 1.384: 1	
3.216: 2.580: 1.862: 1	
3.490: 2.811: 1.958: 1	

$f^3, j=5.4.3.2.1$	$5:4:3:2=2.5:2:1.5:1$
Cr* ... 2.433: 1.971: 1.491: 1	
2.602: 2.138: 1.775: 1	
2.355: 1.959: 1.265: 1	

\* Gieseler arranges the three sets as successive orders of F. But as all the separations are of the same order of magnitude, this may be doubtful—all three are therefore given.

*Seren-folds.*

$p^5, j=4.3.2$	$4:3=1.333:1$
Cr 1.379.	$p^a 1.258$
Mo 1.741;	1.39
Mn <sup>+</sup> 1.490	
$d^7, j=5.4.3.2.1$	$5:4:3:2=2.5:2:1.5:1$
Cr 1.56: 1.24: 1.19: 1	
Mo 2.77: 2.12: 1.49: 1	
$\star 2.758: 2.284: 1.761: 1$	

\* from a multiplet  $p-d$ .

*Four-folds.*

$p^4, j=3.2.1$	$5:3=1.666$	$d^4, j=4.3.2.1$	$7:5:3=2.333:1.666:1$
Mn* 1.750	O <sup>+</sup> 1.51	Mn*	2.541: 1.715: 1

\* Back's new  $pd$  multiplet.

*Six-folds.*

$p^6, j=4.3.2$	$7:5=1.400:1$	$d^6, j=5...1$	$9:7:5:3=$
			[3.000: 2.333: 1.666: 1
Mn S <sup>6</sup>	1.226: 1	Mn. $pd$ (I)	3.151: 2.337: 1.670: 1
S <sup>6a</sup>	1.635: 1	$pd$ (II)	3.346: 2.470: 1.697: 1
$pd$ (III)*	1.574: 1	$dd$ (IV)	2.600: 2.199: 1.295: 1
$dp$ (V)	1.435: 1	$dd$ (VII)	3.385: 2.622: 1.755: 1

\* Roman numerals refer to Catalan's multiplets in his order.

$f^6, j=6...1.$	$11:9:...:3=3.666:3:2.333:1.666:1$
Mn F <sup>6</sup> (VI.)	..... 4.040: 3.345: 2.500: 1.715: 1

*Eight-folds.*

$p^8, j=5.4.3$	$9:7=1.286:1$	$d^8, j=6:5 \dots 2$	$11:9:7:5=$
			$[2.200:1.800:1.400:1$
<b>Mn P<sup>8</sup></b>	..... $1.343:1$	<b>Mn D<sup>8</sup></b>	..... $2.651:1.93:1.31:1$

In forming a judgment on the foregoing perhaps too much weight should not be given to any adverse evidence depending on the extra  $p, d$  terms brought in by the  $dd', pd', pp'$  multiplets. Their Zeeman patterns show that they are typical  $p, d$  terms; they cannot be higher orders of the  $p(1), d(2)$  terms of the P, D series; but their real nature is still to be found \* and may require as noticed under I. a new category. Also little weight can be given to one or two close agreements amongst a larger number of adverse ones in the same set. We find extremely close agreement in the three fold extra  $d$ --given by the A multiplet  $d-d'$ . The three-fold series  $d$ , however, clearly point to a normal ratio of  $5:3$ . The satellites of a first D set are very subject to displacement, and it is perhaps significant that if we use the next order D(3) in Ca and Sr the ratios become  $1.507, 1.532$  respectively, *i. e.* agree with Landé.

The data taken as a whole speak definitely against the rule as even an approximate one. But we should notice the close general agreement that when the rule gives close ratios so do the observed, and when wide, wide. This appears a very strong argument that there is some connexion with reality behind the rule, such for instance as would occur if the  $j$  enter in the way supposed but loaded with some other physical constant—or classifying number.

October 14.

[*Note added in proof sheets.*—Since writing the above I have become acquainted with the paper by Walters on multiplets in Fe (Jour. Wash. Acad. Sc. xiii. 243) and another by Gieseler and Grotrian (*Zsch.-f. Phys.* xxii. 245) in which the nature of the term-types in Walters' multiplets are considered. We find in Fe cases of transitions from one term-species to four others. It is the only case known to me where the  $j$ -transition rule is contravened. Further we

\* I suspect they involve link connexion. That of the Ba L or  $0/3/2$  is certainly so connected. The line  $n=24737$  in Mn—Cat: IV a  $d_1-d_1'$  line—is linked to another  $n=25040$  by  $392.91=\nu_1+\nu_2-.05$ , and no  $p$  term to produce this can occur in the former. Also the sets on p. 157 of his paper beginning with  $30851.44, 30722.19$  are separated by exact  $\nu_2$ —again with no  $p$  term present.



find the multiplets based on a five manifold, and not as we should have expected from the law suggested above, chiefly on seven- and nine-folds. Gieseler and Grotrian give the data referring to Landé's separation law. In the five-folds they find good agreement in one  $p$ , in one  $d$  out of four, fair agreement in one  $f$  out of two. In the three-folds good agreement in one  $f$  out of two and in one  $g$ . In a note added in the proof they give another  $F^5$  multiplet. Here the separation ratios are  $3 : 2 \cdot 21 : 1 \cdot 56 : 1$  compared with a theoretical  $2 \cdot 5 : 2 : 1 \cdot 50 : 1$ .

C. *Note on Vapour Pressures of Monatomic Substances.*

By ALFRED C. EGERTON\*.

FOR the expression of vapour pressure results, various formulæ have been used as approximations to the thermodynamic formula

$$\log_e p = -\frac{\lambda_0}{RT} + \frac{C_p}{R} \log_e T - \int_0^T \frac{dT}{RT^2} \int_0^T C_p dT + \text{constant}.$$

The three-constant Kirchhoff formula

$$\log p = -\frac{B}{T} - C \log T + A,$$

or the four-constant Nernst formula

$$\log p = -\frac{B}{T} + 1 \cdot 75 \log T - \frac{\epsilon T}{R} + A,$$

are frequently employed. The object of the present paper is to point out that a simple linear equation can be used to express the measurements of the vapour pressures of monatomic substances with about equal accuracy.

The specific heat of the solid at ordinary temperatures is about  $3R$ , while that of the vapour is  $2 \cdot 5R$ , so that  $C$  in the Kirchhoff formula becomes  $0 \cdot 5$ , but this only holds in the region where  $C_v$  is  $3R$ .

It is a necessary consequence of the above thermodynamic formula that a linear relationship ( $\log p$  plotted against  $\frac{1}{T}$ ) should approximately hold.

\* Communicated by the Author.

$$\text{If} \quad \left[ \frac{C_p \log T}{R} - \int_0^T \frac{dT}{RT^2} \int_0^T C_p dT \right]$$

is evaluated, using the Debye formula for a range of values of  $\beta\nu$ , the differences ( $\Delta$ ) closely approach a maximum value which is fairly constant over a wide range of temperature. This range is that over which the vapour pressure is appreciable. The vapour pressure equation of a solid substance with monatomic vapour becomes, therefore,

$$\log p = -\frac{\lambda_0}{RT} + (\Delta + C) = -\frac{B}{T} + A'$$

( $C$  being the chemical constant). Table 1. gives  $\Delta$  for various values of  $\beta\nu$  and  $T$ .

The values of  $\frac{1}{2} \log T$  given in the first column show greater divergency from constancy.

The change with temperature of the integrated value for the correction of  $C_v$  to  $C_p$  is insufficient to affect the conclusion.

It may be mentioned that  $\lambda$  is a maximum where  $\frac{\beta\nu}{T} = 2$

(see Phil. Mag. xxxix. p. 14, 1920); below this temperature vapour pressures would become greater than indicated by extrapolation of the linear relation, but in all such cases the pressures would be immeasurably small.

To take the case of cadmium, the theoretical equation between  $400^\circ \text{K.}$  and the melting point  $594^\circ \text{K.}$  would lead to the formula (where  $\beta\nu = 168$  and chemical constant  $1.487$ ):

$$\begin{aligned} \text{at } 400^\circ \text{K. } \log p &= -\frac{\lambda_0}{RT} + 6.505 - 1.762 - 0.029 + 1.487 \\ &= -\frac{\lambda_0}{RT} + 6.201, \end{aligned}$$

$$\begin{aligned} \text{at } 594^\circ \text{K. } \log p &= -\frac{\lambda_0}{RT} + 6.935 - 2.210 - 0.052 + 1.487 \\ &= -\frac{\lambda_0}{RT} + 6.159. \end{aligned}$$

Taking  $\log p \text{ mm.} = -2.33$  at  $523^\circ \text{K.}$ , the thermodynamic equation might be expressed very closely by

$$\log p \text{ (atmos.)} = -\frac{5954}{T} + 6.287 - 2.14 \cdot 10^{-4} T.$$

TABLE I.

T° K.	Differences $\Delta$ .									
	$\frac{1}{2} \log T.$	$2\frac{1}{2} \log T.$	$\beta = 20.$	$= 50.$	$= 100.$	$= 200.$	$= 300.$	$= 400.$	$= 500.$	$= 1000.$ $= 2000.$
10	0.5	2.500	2.1194	2.4401	2.4916					
20	0.65	3.2525	2.2614	2.9875	3.1926	3.2441	3.2500			
50	0.8465	4.2475	2.4311	3.3504	3.8669	4.1446	4.2106	4.2311	4.2391	
100	1.0	5.0000	2.3749	3.4284	4.1089	4.6194	4.8106	4.8971	4.9101	4.9916
200	1.1505	5.7525	2.2727	3.3919	4.1809	4.8614	5.1914	5.3719	5.4875	5.6926
400	1.3010	6.5052	2.1476	3.2746	4.1446	4.9336	5.3511	5.6141	5.7828	6.2402
600	1.3891	6.9455	...	...	4.0658	4.9149	5.3739	5.6756	5.8876	6.4526
800	1.4515	7.2577	...	...	4.0271	4.8971	5.3626	5.6861	5.9222	6.5550
1000	1.5000	7.5000	...	...	4.0202	4.8749	5.3657	5.6836	5.9284	6.7089
1500	1.5880	7.9402	...	...	...	4.7801	5.3151	5.6582	5.9096	6.6703
2000	1.6505	8.2525	...	...	...	4.7727	5.2192	5.6274	5.8919	6.6809
3000	1.7385	8.6927	...	...	...	4.6863	5.2129	5.5452	5.8140	6.6621

The following Table (II.) shows that this equation leads to very nearly the same results as the empirically determined linear equation  $\log p \text{ atmos.} = -\frac{5891}{T} + 6.053$ .

TABLE II.

T.	log p.		
	Thermodynamic.	Empirical.	Observed.
421.9	-5.035	-5.028	-4.96
482.6	-3.273	-3.272	-3.28
513.6	-2.536	-2.536	-2.54
523.0	-2.329	-2.329	-2.33
532.5	-2.128	-2.129	-2.12
545.6	-1.863	-1.864	-1.88

At high and low temperatures greater divergencies might be expected, but it is possible to represent over the range of the measurements the vapour pressure of solid argon and of tungsten by a linear relation as well as by any other equation, as the following figures illustrate :—

TABLE III A.—Vapour Pressure of Argon (Solid).

T° K.	I.	II.	III.	IV.
65.49	1.3418	1.3387	1.3414	1.3395
66.16	1.4041	1.4000	1.4024	1.4016
69.43	1.6809	1.6944	1.6941	1.6996
70.49	1.7727	1.7843	1.7833	1.7893
71.95	1.8891	1.8988	1.8972	1.9044
73.93	2.0483	2.0541	2.0517	2.0590
75.50	2.1644	2.1645	2.1623	2.1695
76.69	2.2477	2.2544	2.2515	2.2605
77.48	2.3023	2.3035	2.3010	2.3093
79.06	2.4075	2.4098	2.4073	2.4146
80.60	2.5068	2.5079	2.5057	2.5111
81.42	2.5569	2.5569	2.5551	2.5600
82.75	2.6394	2.6428	2.6408	2.6449
83.21	2.6668	2.6673	2.6657	2.6697
83.93	2.7095	2.7082	2.7070	2.7100

Column I. Measurements by Born (*Ann. d. Phys.* lxi. p. 473, 1922).

Column II.  $\log p = -\frac{408.80}{T} + 7.5811$ .

Column III.  $\log p = -\frac{366.87}{T} + 1.75 \log T - .0028293 T + 1.0698$ .

Nernst formula used by Born.

Column IV.  $\log p = -\frac{401.88}{T} + 2.5 \log T - F(\beta\nu) + .0000142 T^2 + 3.671$

taking  $\beta\nu=85$ ,  $\lambda_0=1840$ ,  $C=3.67$ .

TABLE III B.

## Vapour Pressure of Tungsten.

T° K.	I.	II.	III.	IV.
2440	-6.903	-6.990	-6.972	-6.648
2522	-6.426	-6.370	-6.359	-6.113
2300	-4.583	-4.544	-4.542	-4.535
2930	{ -3.900 } { -3.766 }	-3.809	-3.814	-3.903
2925	{ -3.929 } { -3.798 }	-3.836	-3.842	-3.928
3136	-2.673	-2.772	-2.781	-3.014

Column I. Measurements of Langmuir (*Phys. Zeit.* xiv. p. 1273, 1913).

Column II.  $\log p = 15.502 - \frac{47440}{T} - 0.9 \log T$ .

Column III.  $\log p = 11.920 + \frac{46100}{T}$ .

Column IV.  $\log p = -\frac{41.311}{T} + 7.835 - 1.78 \cdot 10^{-4} T$ .

(Assuming  $C = 1.808$ ;  $\beta r = 300$ .)

In the case of tungsten the approximate thermodynamic formula (column IV.) so far as it can be derived from the specific heat measurements of Worthing, does not agree well with the experimental results, which are expressed quite as well linearly as by the Hertz formula employed by Langmuir. It is clear that vapour pressure measurements alone are generally insufficient for the determination of  $\lambda_0$ , without accurate knowledge of the variation of specific heats with temperature.

Since the change of specific heat of a supercooled liquid is not known precisely, the thermodynamic equation for the vapour pressure of a liquid

$$\ln p_T^l = -\frac{\lambda_0^s}{RT} - \left[ \frac{1}{R} - \int_0^{T_m} \frac{C_p^s dT}{R} - \int_0^{T_m} \frac{C_p^l dT}{R} \right] \frac{T - T_m}{T_m} \\ + \frac{C_p^g}{R} \ln T - \int_{T_m}^T \frac{dT}{RT^2} \int_{T_m}^T C_p^l dT - \int_0^{T_m} \frac{dT}{RT^2} \int_0^{T_m} C_p^l dT + C$$

cannot readily be evaluated. In order to obtain the true value of  $\lambda_0^s$  and  $C$ , the vapour pressure has usually to be extrapolated to the melting point, and in the case of the molten elements it is generally sufficient to extrapolate by means of a linear equation.

The following linear equations are found to hold as closely as any three-constant formulæ in the following cases :—

$$\text{Zinc :} \quad \log p = -\frac{6170}{T} + 8.107$$

(cf. Braune's Measurements, *Zeit. Anorg. Chem.* cxi. p. 109, 1920).

$$\text{Lead :} \quad \log p = -\frac{10265}{T} + 8.3165$$

(cf. Ingold's Measurements, *J. C. S.* cxxi. p. 2419, 1922).

$$\log p = -\frac{9923}{T} + 7.903 \text{ or } \frac{10350}{T} + 8.347$$

(Egerton, *Proc. Roy. Soc.* ciii. p. 469, 1923).

$$\text{Cesium :} \quad \log p = -\frac{3753}{T} + 7.256$$

(Scott, *Phil. Mag.* xlvii. p. 32, 1924).

$$\text{Rubidium :} \quad \log p = -\frac{4209}{T} + 7.331 \quad (\text{Ibid.}).$$

In the case of mercury, the linear relation

$$\log p = -\frac{3252.2}{T} + 8.1691$$

accords well with the measurements of Knudsen, and

$$\log p = -\frac{3117.5}{T} + 7.8300$$

with those of Smith and Menzies; it has already been pointed out (*Phil. Mag.* xxxix. p. 1, 1920) that the two careful sets of measurements do not agree well with each other, and experiments are being made to find out where the discrepancy lies.

The equations

$$\log p = -\frac{B'}{T} + A' \text{ or } \log p = -\frac{B}{T} - C \log T + A''$$

$$\text{or } \log p = -\frac{\lambda_0}{RT} + A'' + C''T$$

(where  $C$  and  $C''$  have nearly the same values for all elements), lead necessarily to the Ramsay and Young equation

$$\frac{T_1'}{T_2'} = \frac{T_1}{T_2} + K(T_1' - T_1),$$

where  $K$  in the case of the 1st equation would be given by

$$\frac{A_2' - A_1'}{B_2' - B_1'} R$$

( $T_1$  and  $T_2$  are the temperatures of equal vapour pressure for two different substances).

Ingold (J. C. S. cxxi. p. 2419, 1922) has claimed for molten lead that the Ramsay-Young equation gives closer agreement than is obtained by extrapolation of the four-constant Nernst equations. Since the formulæ above cited (particularly the last) are very close approximations to the thermodynamic formula, the Ramsay and Young equation naturally should hold. Having fixed the vapour pressure of a certain metal, that of other metals can be found if one point on the vapour pressure line is fixed by careful measurement and consequently with some approximation  $\lambda_0$  and the other thermal constants which enter into the thermodynamic vapour pressure formula.

*Summary.*

1. On the basis of the thermodynamic vapour pressure formula a linear equation  $\log p = -\frac{a}{T} + b$  closely represents the variation of vapour pressure with temperature of a solid with monatomic vapour.

2. Various examples are given of the application of this equation.

3. A vapour pressure determination at a single temperature should suffice to determine the course of the whole curve.

Clarendon Laboratory,  
Oxford.

CI. *The Thermal Conductivity of Solid Electric Insulators.*

—II. By W. M. THORNTON, *Professor of Electrical Engineering, Armstrong College, Newcastle-upon-Tyne* \*.

1. IN a review of Debye's theory of the atomic heats of solids Jeans remarks †:—"Debye's result may be summarised in the statement that the whole heat-energy of an element resides in the energy of its elastic-solid vibrations, the atoms being treated as particles of the solid, and each vibration having exactly the energy allotted to it by the quantum-theory." It follows that the continuous transmission of heat through insulating solids proceeds in the same way.

For many electrical insulators the thermal conductivity  $k$  is proportional to the product of the longitudinal elasticity  $E$  and

\* Communicated by the Author.

† Report on Radiation and the Quantum-Theory by J. H. Jeans, 2nd ed. §61, p. 60.

the density  $\rho$ , and  $k = E\rho \cdot 10^{-14}$  for widely different substances\*. The rate of transmission of the elastic vibrations which constitute heat in solids is then proportional to the force between molecules of which elasticity is a measure. According to Nernst, Debye's formula for molecular heat takes account of the vibrations of the molecules, Einstein's of the atoms. The above relation supports this to the extent that for  $k$  to be proportional to  $E$  one of them must deal with molecular forces, and Einstein's professedly does not.

Expressing the heat  $k$  in mechanical units as  $\frac{mv^2}{J}$ ,  $v$  is the difference of the mean square velocities of vibration between opposite sides of unit cube across which unit temperature gradient is maintained. The mass is numerically the density of the substance, so that  $k = E\rho = \rho v^2/J$ . The velocity of molecular heat vibration therefore follows the same law as that of sound, in that  $v^2$  varies as the elasticity in the direction of transmission. This is the meaning of the relation between  $k$ ,  $E$ , and  $\rho$ , given in the previous paper, which should therefore be true for all substances in which heat is transmitted by vibration of molecules, or of atoms when the energy of the latter bears a constant ratio to the former, as it does at normal temperatures.

2. In the case of graphite,  $E = 5.2 \cdot 10^{11}$ ,  $v^2 = EJ \cdot 10^{-14}$ , and  $v = 460$  centimetres a second, increase of molecular velocity per degree rise of temperature. The average velocity for simple harmonic vibrations is 0.9 the root mean square value, and is 4 times the product of frequency and amplitude. At temperatures approaching the infra-red, with atomic frequencies about  $10^{12}$ , the corresponding change of amplitude is in the case of graphite  $10^{-10}$  centimetre, less than a hundredth of a molecular diameter, per degree, a not improbable value for atomic vibrations.

Molecular movement in solids at speeds equivalent to a frequency of the order of  $10^{13}$  occurs in the passage of sound. When the molecules in the wave-front are all in phase the motion is transmitted as sound; when they are in complete confusion, as heat, the elastic movement being the same in both cases.

3. Variations from the relation  $k = E\rho$  have been pointed out by Clarke† in the case of certain glasses. The values

\* "The Thermal Conductivity of Solid Insulators," *Phil. Mag.* xxxviii. p. 705, Dec. 1919.

† "The Thermal Conductivity of some Insulators," J. R. Clarke, *Phil. Mag.* xl. p. 502 (1920).



of  $k$ , calculated from observed elastic constants and densities, are in some cases higher, in others lower than if the relation were independent of composition. In the light of modern knowledge of molecular structure, glasses are complex interlaced lattices. The elasticity of the whole is not a known function of the forces within the molecule. When the thermal conductivity calculated from  $E\rho$  is less than the observed value it may be accepted as an indication that the solid as a whole has less elasticity than its elements, or that the atomic vibrations which undoubtedly add to molecular heat, and are not so far as we know directly related to the elasticity  $E$ , retard by absorption the transmission of energy. When, on the other hand, the observed value of  $k$  is greater than  $E$  the interlocked lattices form a structure stiffer than the transmitted heat vibrations indicate.

Optical glasses are not, as Clarke states, very suitable for testing the validity of the relationship  $k=E\rho$ , though the agreement is in some cases close. Their composition is usually much more complex than that of the other insulators considered. Taking the Jena glasses 19 to 38 discussed by him, eleven have a thermal conductivity greater than  $E\rho$ , five have less. For all these the ratio  $\frac{\Sigma(k)_{\text{obs.}}}{\Sigma(E\rho)}=1.3$ . The longitudinal elasticity is on the whole less than that by which heat movement is transmitted.

CII. *The Principle of Equivalence in the Theory of Relativity.*  
*By* TRACY YERKES THOMAS, *National Research Fellow in Mathematical Physics, Department of Physics, University of Chicago* \*.

1. *Introduction.*

IN considering the propagation of light in a gravitational field in 1911, Einstein† made the assumption that a homogeneous gravitational field is completely equivalent to a uniform acceleration of the coordinate system. This assumption is Einstein's *original* principle of equivalence. As thus stated, however, the principle applies only to the case of a homogeneous gravitational field, and is consequently unsuited for the requirements of the general theory of relativity.

\* Communicated by the Author.

† A. Einstein, "Über den Einfluss der Schwerkraft auf die Ausbreitung des Lichtes," *Ann. d. Physik*, xxxv. p. 898 (1911).

Accordingly, in his formulation of the general theory of relativity in 1916, Einstein \* replaced the above statement of the principle of equivalence by the assumption that the special theory of relativity holds in an infinitely small four-dimensional region for a proper choice of coordinates. This modification of his original assumption has retained the name of the principle of equivalence. The proper choice of coordinates is considered to be one for which the linear element or interval has the same form as in the special theory of relativity for some point in the infinitely small four-dimensional region. Beyond this, no definite specification of coordinates is made. This statement of the principle of equivalence furnishes a means by which we may pass from the laws of the special theory of relativity to those of the general theory. The principle suggests that the laws of the special theory of relativity when expressed in a form which is invariant under arbitrary transformations of coordinates will retain this form for the general theory of relativity. But, as has been pointed out by Eddington †, this method of generalization from a flat to a curved manifold cannot always be expected to lead to correct results. For if the general law depends on terms involving the curvature of the world, these terms will not be determined by such a method of generalization, since the curvature tensor vanishes identically in the special theory of relativity.

In this paper we give a statement of the principle of equivalence by means of *point-inertial* systems of coordinates. These systems are very closely related to the ordinary inertial systems of the special theory of relativity, and reduce to the latter in case the gravitational field can be removed by a transformation of coordinates. Point-inertial systems appear to be the "proper choice of coordinates" mentioned by Einstein in his later statement of the principle of equivalence. Their use gives a *unique* determination of the general laws from those of the special theory of relativity.

We assume the Riemann geometry as specified by the condition (2.3). It should be observed, however, that our statement of the principle of equivalence does not depend on the condition (2.3), but only on the existence of a fundamental metric tensor  $g_{\alpha\beta}$  satisfying (5.2). This raises the question if it is not possible to apply the principle of equi-

\* A. Einstein, "Die Grundlagen der allgemeinen Relativitätstheorie," *Ann. d. Physik*, vol. xlix. p. 769 (1916).

† A. S. Eddington, 'The Mathematical Theory of Relativity,' p. 40 (1923).

valence to this more general metric geometry, on the basis of which Einstein \* has recently considered a new insertion of electricity in the theory of relativity. But such an application of the principle of equivalence has not been attempted in the present article.

## 2. Riemann Geometry.

We consider a system of paths,

$$x^i = \psi^i(s), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.1)$$

which take the place of the straight lines of euclidean geometry, and which are given as solutions of the set of differential equations † :

$$\frac{d^2 x^i}{ds^2} + \Gamma_{\alpha\beta}^i \frac{dx^\alpha}{ds} \frac{dx^\beta}{ds} = 0. \quad . \quad . \quad . \quad . \quad (2.2)$$

The  $\Gamma$ 's in these equations are Christoffel symbols with respect to a symmetric tensor  $g_{\alpha\beta}$ ; i. e.,

$$g_{\alpha\beta, \gamma} = 0, \quad . \quad . \quad . \quad . \quad . \quad (2.3)$$

where  $g_{\alpha\beta, \gamma}$  denotes the covariant derivative of  $g_{\alpha\beta}$ . Under an arbitrary analytic transformation of coordinates,

$$x^i = g^i(\bar{x}), \quad . \quad . \quad . \quad . \quad . \quad (2.4)$$

which may also be written

$$x^i = f^i(x), \quad . \quad . \quad . \quad . \quad . \quad (2.5)$$

the differential equations (2.2) of the paths (2.1) become

$$\frac{d^2 x^i}{ds^2} + \bar{\Gamma}_{\alpha\beta}^i \frac{dx^\alpha}{ds} \frac{dx^\beta}{ds} = 0. \quad . \quad . \quad . \quad . \quad (2.6)$$

It follows from (2.3) that the  $\bar{\Gamma}$ 's are Christoffel symbols with respect to the tensor  $\bar{g}_{\alpha\beta}$ , into which the tensor  $g_{\alpha\beta}$  is transformed by the transformation (2.4).

It can be shown that (2.3) is a sufficient condition for the paths (2.1) to possess the homogeneous quadratic first integral

$$g_{\alpha\beta} \frac{dx^\alpha}{ds} \frac{dx^\beta}{ds} = \mu^2, \quad . \quad . \quad . \quad . \quad (2.7)$$

where  $\mu^2$  is a constant for any particular path.

\* Cf. the series of notes by A. Einstein in the *Berlin Sitzungsberichte* (1923).

† L. P. Eisenhart and O. Veblen, 'The Riemann Geometry and its Generalization,' *Proc. Nat. Acad. Sci.* vol. viii. p. 19 (1922).

We define the length  $l$  of a curve  $c$  extending between the points  $(x_0)$  and  $(x_1)$  by

$$l = \int_{x_0}^{x_1} \sqrt{g_{\alpha\beta} \frac{dx^\alpha}{dt} \frac{dx^\beta}{dt}} dt, \quad . \quad . \quad . \quad (2.8)$$

where  $t$  is the parameter occurring in the parametric representation of the curve  $c$ . In case the curve  $c$  is a path (2.1), the length  $l$  becomes

$$l = \int_{s_0}^{s_1} \mu ds = \mu(s_1 - s_0). \quad . \quad . \quad . \quad (2.9)$$

It follows from (2.8) that the linear element  $dl$  is given by :

$$dl^2 = g_{\alpha\beta} dx^\alpha dx^\beta. \quad . \quad . \quad . \quad (2.10)$$

The paths of zero length, which are light tracks in the theory of relativity, correspond to  $\mu=0$ . Paths which are not of zero length are geodesics—i. e., they are the curves for which the integral

$$\int_{x_0}^{x_1} \sqrt{g_{\alpha\beta} \frac{dx^\alpha}{dt} \frac{dx^\beta}{dt}} dt \quad . \quad . \quad . \quad (2.11)$$

is stationary.

### 3. Normal Coordinates\*.

A unique solution (2.1) of the differential equations (2.2) is determined by a set of initial conditions :

$$x^i = p^i \text{ when } s = 0, \quad . \quad . \quad . \quad (3.1)$$

$$\frac{dx^i}{ds} = \xi^i \text{ when } s = 0. \quad . \quad . \quad . \quad (3.2)$$

This solution is of the particular form

$$x^i = p^i + \Gamma^i(p, \xi s). \quad . \quad . \quad . \quad (3.3)$$

Let us now put

$$y^i = \xi^i s. \quad . \quad . \quad . \quad (3.4)$$

Then the equations (3.3) become

$$x^i = p^i + \Gamma^i(p, y), \quad . \quad . \quad . \quad (3.5)$$

and these equations determine a transformation from the coordinates  $(x)$  to a new set of coordinates  $(y)$ . The  $(y)$  coordinates defined by (3.5) are called *normal coordinates*.

\* O. Veblen, "Normal Coordinates for the Geometry of Paths," Proc. Nat. Acad. Sci. vol. viii. p. 192 (1922).

A path (2.1) satisfying the initial conditions (3.1) and (3.2) is given by (3.4) in normal coordinates. Hence, if the functions  $\Gamma_{\alpha\beta}^i$  are denoted by  $C_{\alpha\beta}^i$  when transformed to a system of normal coordinates ( $y$ ), the  $C$ 's satisfy the condition

$$(C_{\alpha\beta}^i)_0 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.6)$$

at the origin of normal coordinates.

It can be shown that under an arbitrary transformation of the ( $x$ ) coordinates the normal coordinates ( $y$ ) which are defined by the ( $x$ ) coordinates and a point  $p$  suffer a linear homogeneous transformation with constant coefficients\*. We may therefore determine a system of normal coordinates ( $y$ ) at the origin of which (2.10) has the form

$$dl^2 = a_\alpha dy^\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.7)$$

where the  $a$ 's are either  $\pm 1$ . In case the  $a$ 's are all  $+1$ , these normal coordinates are determined to within an orthogonal transformation.

#### 4. Extension of Tensors†.

Let us denote by  $T_{ij\dots k}^{lm\dots n}$  an arbitrary tensor which is contravariant in the indices ( $l, m, \dots, n$ ) and covariant in the indices ( $i, j, \dots, k$ ). Let us then define a set of functions  $T_{ij\dots k, p\dots q}^{lm\dots n}$  of ( $x$ ) by

$$T_{ij\dots k, p\dots q}^{lm\dots n} = \left( \frac{\partial^n T_{ij\dots k}^{lm\dots n}}{\partial y^p \dots \partial y^q} \right)_0, \quad . \quad . \quad . \quad . \quad (4.1)$$

where the derivative is evaluated at the origin of a system of normal coordinates ( $y$ ). It can be shown that  $T_{ij\dots k, p\dots q}^{lm\dots n}$  is a tensor which is contravariant in the indices ( $l, m, \dots, n$ ) and covariant in the indices ( $i, j, \dots, k, p, \dots, q$ ). We shall call this tensor the  $n$ th extension of  $T_{ij\dots k}^{lm\dots n}$ , provided that there are  $n$  indices ( $p, \dots, q$ ).

The first extension of any tensor is the ordinary covariant derivative of the tensor. However, the second extension of a tensor is not the same as the ordinary second covariant derivative of the tensor, and in general the  $n$ th extension ( $n > 1$ ) is not the same as the ordinary  $n$ th covariant derivative of the tensor. Lists of formulæ of extension, together with formulæ giving the relations between various extensions, are given in the 'Geometry of Paths' (*loc. cit.*).

\* O. Veblen and T. Y. Thomas, "The Geometry of Paths," Trans. Am. Math. Soc. vol. xxv. p. 551 (1923).

† O. Veblen and T. Y. Thomas, *loc. cit.*

For example, the second extensions of the covariant vector  $T_i$  and the covariant tensor  $T_{ij}$  are :

$$T_{i,pq} = \frac{\partial^2 T_i}{\partial x^p \partial x^q} - \frac{\partial T_i}{\partial x^a} \Gamma_{pq}^a - \frac{\partial T_a}{\partial x^p} \Gamma_{iq}^a - \frac{\partial T_a}{\partial x^q} \Gamma_{ip}^a - T_a \Gamma_{ipq}^a, \quad . \quad . \quad (4.2)$$

$$T_{ij,pq} = \frac{\partial^2 T_{ij}}{\partial x^p \partial x^q} - \frac{\partial T_{ij}}{\partial x^a} \Gamma_{pq}^a - \frac{\partial T_{aj}}{\partial x^p} \Gamma_{iq}^a - \frac{\partial T_{ia}}{\partial x^p} \Gamma_{jq}^a - \frac{\partial T_{aj}}{\partial x^q} \Gamma_{ip}^a \\ - \frac{\partial T_{ia}}{\partial x^q} \Gamma_{jp}^a - T_{aj} \Gamma_{ipq}^a - T_{ia} \Gamma_{jpq}^a + T_{a\beta} \Gamma_{ip}^a \Gamma_{jq}^\beta + T_{a\beta} \Gamma_{iq}^a \Gamma_{jp}^\beta, \quad . \quad . \quad (4.3)$$

in which

$$\Gamma_{jkl}^i = \frac{1}{3} \left( \frac{\partial \Gamma_{jk}^i}{\partial x^l} + \frac{\partial \Gamma_{kl}^i}{\partial x^j} + \frac{\partial \Gamma_{lj}^i}{\partial x^k} - 2\Gamma_{aj}^i \Gamma_{kl}^a - 2\Gamma_{ak}^i \Gamma_{lj}^a - 2\Gamma_{al}^i \Gamma_{jk}^a \right). \quad (4.4)$$

The second extensions  $T_{i,pq}$  and  $T_{ij,pq}$  are related to the second covariant derivatives  $T_{i,p,q}$  and  $T_{ij,p,q}$  respectively by the formulæ :

$$T_{i,p,q} = T_{i,pq} - T_a A_{ipq}^a, \quad . \quad . \quad . \quad (4.5)$$

$$T_{ij,p,q} = T_{ij,pq} - T_{aj} A_{ipq}^a - T_{ia} A_{jpq}^a, \quad . \quad . \quad (4.6)$$

where the  $A$ 's are normal tensors.

### 5. Point-inertial Systems.

The special theory of relativity deals with a particular class of coordinate systems called inertial systems. These systems are characterized by the fact that the interval  $dl$  has the particular form,

$$dl^2 = dt^2 - dx^2 - dy^2 - dz^2, \quad . \quad . \quad . \quad (5.1)$$

where  $t$  denotes the time and  $(x, y, z)$  are the coordinates of a rectangular coordinate system. All inertial systems having their origins at a common point are related by a linear homogeneous transformation of the variables with constant coefficients called the Lorentz transformation, which possesses the property that it leaves the form (5.1) invariant. The invariance of (5.1) under the Lorentz transformation expresses the fact that a light-ray has a constant velocity (which we here take to be unity) in all inertial systems.

We make the assumption in the general theory of relativity that the metric is such that the  $a$ 's in (3.7) have the values  $a_0 = 1, a_1 = a_2 = a_3 = -1$ . Hence 3.7 becomes

$$dl^2 = dy_0^2 - dy_1^2 - dy_2^2 - dy_3^2. \quad . \quad . \quad . \quad (5.2)$$

The system of normal coordinates  $(y^0, y^1, y^2, y^3)$  at the origin

of which (5.2) holds is determined to within a Lorentz transformation.

We shall call the system of normal coordinates  $(y^0, y^1, y^2, y^3)$  a *point-inertial* system, on account of the similarity between these systems and the ordinary inertial systems of the special theory of relativity\*. If there exists a transformation changing (2.10) into the form (5.2), this will be accomplished by the transformations leading to the point-inertial system, so that in such a case the form (5.2) will hold throughout the point-inertial system.

For convenience we shall also denote by  $(t, x, y, z)$  the coordinates of a point-inertial system. In this case the form (5.1) will hold at the origin of the point-inertial system.

The following properties of point-inertial systems relating these systems to the inertial systems of the special theory of relativity may readily be verified.

In the special theory :—

(1) The interval  $dl$  has the form (5.1) *throughout* the inertial system.

(2) The functions  $\Gamma_{\alpha\beta}^i$  vanish *throughout* the inertial system.

(3) Light is propagated with the velocity unity *throughout* and relatively to all inertial systems.

(4) The covariant derivative is equal to the ordinary partial derivative *throughout* the inertial system. In general the  $n$ th extension is equal to the  $n$ th partial derivative *throughout* the inertial system.

(5) The equations of a path passing through the origin of the inertial system are of the form (3.4).

(6) Inertial systems having their origins at a common point are related by the homogeneous Lorentz transformation.

In the general theory :—

(1) The interval  $dl$  has the form (5.1) *at the origin* of the point-inertial system.

(2) The functions  $\Gamma_{\alpha\beta}^i$  vanish *at the origin* of the point-inertial system †.

(3) Light is propagated with the velocity unity *at the origin* of and relatively to all point-inertial systems.

(4) The covariant derivative is equal to the ordinary partial derivative *at the origin* of the point-inertial system. In general the  $n$ th extension is equal to the  $n$ th partial derivative *at the origin* of the point-inertial system.

(5) The equations of a path passing through the origin of the point-inertial system are of the form (3.4).

(6) Point-inertial systems having their origins at a common point are related by the homogeneous Lorentz transformation.

\* Cf. G. N. Birkhoff, 'Relativity and Modern Physics,' p. 118, § 7 (1923).

† It follows from the condition (2.3) that the first derivatives of  $g_{\alpha\beta}$  vanish at the origin of the point-inertial system.

This comparison clearly shows that the point-inertial systems of the general theory of relativity are very closely related to the inertial systems of the special theory.

### 6. *Principle of Equivalence.*

The results of the preceding section suggest that the special theory of relativity will hold for an observer at the origin of the point-inertial system—i. e., that the measurements of such an observer will have the significance of measurements of space and time in the special theory of relativity. We are thus led to consider that some of the laws (invariant equations) of the general theory of relativity will have the exact form of the corresponding laws of the special theory of relativity when referred to the origin of the point-inertial system. This assumption will be spoken of as the principle of equivalence. It will not be possible for every law of the general theory of relativity to assume the form of the corresponding law in the special theory at the origin of the point-inertial theory, as this would involve inconsistencies in the general laws. However, to every law of the special theory of relativity there will be a law of the general theory, which will be uniquely determined from the law of the special theory by means of the principle of equivalence.

The remaining sections of this paper will be devoted to particular applications of the principle of equivalence.

### 7. *Propagation of a Potential.*

The wave equation

$$\frac{\partial^2 \phi}{\partial t^2} - \frac{\partial^2 \phi}{\partial x^2} - \frac{\partial^2 \phi}{\partial y^2} - \frac{\partial^2 \phi}{\partial z^2} = 0 \quad . \quad . \quad . \quad (7.1)$$

expresses the fact that the potential  $\phi$  is propagated with the velocity of light unity. According to the principle of equivalence, this equation is to be introduced into the general theory of relativity by requiring that it be satisfied at the origin of the point-inertial system. As is customary, we denote by  $g^{\alpha\beta}$  the cofactor of the corresponding  $g_{\alpha\beta}$  in the determinant

$$g = \begin{vmatrix} g_{11} & \dots & g_{14} \\ g_{41} & \dots & g_{44} \end{vmatrix}, \quad . \quad . \quad . \quad (7.2)$$

divided by the determinant  $g$ . Then  $g^{\alpha\beta}$  constitutes a contravariant symmetric tensor, and the equation (7.1)



which holds at the origin of the point-inertial system can be written in the invariant form

$$g_{\alpha\beta}\phi_{,\alpha\beta} = 0, \quad . \quad . \quad . \quad . \quad . \quad (7.3)$$

where  $\phi_{,\alpha\beta}$  is the second extension of the potential  $\phi^*$ .

Let us denote by  $\square$  the operation of forming the second extension of a scalar, vector, or tensor, and then contracting the indices of extension by multiplication with  $g^{\alpha\beta}$ . Thus, in general,

$$\square T_{ij\dots k}^{lm\dots n} = g^{\alpha\beta} T_{ij\dots k, \alpha\beta}^{lm\dots n}, \quad . \quad . \quad . \quad . \quad (7.4)$$

where  $T_{ij\dots k, \alpha\beta}^{lm\dots n}$  is the second extension of the tensor  $T_{ij\dots k}^{lm\dots n}$ .

The equation (7.3) may now be written

$$\square\phi = 0. \quad . \quad . \quad . \quad . \quad . \quad (7.5)$$

Hence, according to the principle of equivalence, the wave equation (7.1) takes the form (7.5) when introduced into the general theory of relativity.

### 8. Conservative Equations.

According to the principle of equivalence, the laws of conservation of energy and momentum will hold in the ordinary sense for the observer at the origin of the point-inertial system. This assumption has its expression in the equations

$$\frac{\partial \mathcal{S}_\nu^\mu}{\partial y^\mu} = 0 \quad . \quad . \quad . \quad . \quad . \quad (8.1)$$

referred to the origin of the point-inertial system, where  $\mathcal{S}_\nu^\mu = \sqrt{-g} T_\nu^\mu$  is the tensor density of the energy tensor  $T_\nu^\mu$  and depends on the energy density of the electromagnetic field and ponderable matter. On account of the condition (2.3), the equations (8.1) become

$$\frac{\partial T_\nu^\mu}{\partial y^\mu} = 0, \quad . \quad . \quad . \quad . \quad . \quad (8.2)$$

also referred to the origin of the point-inertial system. We do not know the exact form of the tensor  $T_\nu^\mu$  inside the elementary electrical charges, but a form which is sufficiently accurate for many purposes is given by

$$T_\nu^\mu = \rho g_{\nu\sigma} \xi^\sigma \xi^\mu, \quad . \quad . \quad . \quad . \quad (8.3)$$

\* The second extension and the second covariant derivative of a scalar function  $\phi$  are identical.

where  $\rho$  denotes the stationary density of matter and  $\xi^\sigma$  is a vector which is equal to  $\frac{dx^\sigma}{ds}$  along any world-line. Inserting (8.3) into the conservation equations (8.2), we obtain well-known equations of hydrodynamics\*.

Transforming the equations (8.1) to arbitrary coordinates, we obtain

$$\frac{\partial \mathcal{G}^\mu}{\partial x^\mu} - \Gamma_{\nu\tau}^\sigma \mathcal{G}_\sigma^\tau = 0. \quad . \quad . \quad . \quad . \quad (8.4)$$

Hence, according to the principle of equivalence the equations (8.4) express the laws of conservation in the general theory of relativity.

### 9. Gravitational Equations.

We assume that the gravitational potentials  $g_{\mu\nu}$  are propagated with the velocity of light in the ordinary galilean sense for the observer at the origin of the point-inertial system. We meet this requirement by putting

$$\square g_{\mu\nu} = \psi_{\mu\nu}, \quad . \quad . \quad . \quad . \quad (9.1)$$

where  $\psi_{\mu\nu}$  is a symmetric "tensor of matter" which, like the energy tensor  $T_{\mu\nu}^*$ , may be assumed to depend on the energy density of the electromagnetic field and ponderable matter. For at the origin of the point-inertial system (9.1) becomes

$$\frac{\partial^2 g_{\mu\nu}}{\partial t^2} - \frac{\partial^2 g_{\mu\nu}}{\partial x^2} - \frac{\partial^2 g_{\mu\nu}}{\partial y^2} - \frac{\partial^2 g_{\mu\nu}}{\partial z^2} = \psi_{\mu\nu}, \quad . \quad . \quad . \quad (9.2)$$

and the ordinary solution of an equation of this form involving retarded potentials will therefore apply at the origin of the point-inertial system. Hence the observer at the origin of the point-inertial system will consider that the gravitational potentials  $g_{\mu\nu}$  are propagated with the velocity of light unity†.

If space were euclidean, then the  $\Gamma$ 's would vanish throughout the point-inertial system. In reality space is not euclidean, although its actual deviation from the euclidean is very slight; we therefore assume that space is euclidean

\* Cf. A. S. Eddington, *loc. cit.* p. 117.

† A similar treatment may evidently be given for electromagnetic waves. This would lead to equations of the form  $\square \phi_{\mu\nu} = \theta_{\mu\nu}$ , where  $\phi_{\mu\nu}$  is the skew-symmetric electromagnetic tensor and  $\theta_{\mu\nu}$  is a skew-symmetric tensor of matter.

to the extent that the  $\Gamma$ 's and their first derivatives are negligibly small in the point-inertial system. The  $g$ 's will differ but slightly from the galilean values in the point-inertial system, and the gravitational equations (9.1) will therefore take the form (9.2) very approximately throughout this system. We thus arrive at an approximate theory of gravitational waves very similar to that given by Einstein \*. But the principle of equivalence gives an exact theory of the propagation of gravitational waves. For, according to this principle, the gravitational equations (9.1) express the fact that the gravitational potentials  $g_{\mu\nu}$  are propagated with the velocity of light for the observer at the origin of the point-inertial system, the only place where we can speak of a velocity of propagation in the ordinary sense.

We obtain the Einstein gravitational equations from (9.1) if we assume that these equations contain the equations of conservation (8.2). This assumption may be satisfied by putting

$$\psi_{\mu\nu} = k(T_{\mu\nu} - \frac{1}{2}g_{\mu\nu}T), \quad . \quad . \quad . \quad (9.3)$$

in which

$$T_{\mu\nu} = g_{\mu\sigma}T_{\nu}^{\sigma},$$

$$T = g^{\mu\nu}T_{\mu\nu},$$

and  $k$  is a constant. By the substitution (9.3), we have

$$\square g_{\mu\nu} = k(T_{\mu\nu} - \frac{1}{2}g_{\mu\nu}T). \quad . \quad . \quad . \quad (9.4)$$

To prove that the equations (9.4) yield the conservation equations (8.2), we shall transform these equations into the ordinary Einstein equations of the gravitational field, namely :

$$R_{\mu\nu} - \frac{1}{2}g_{\mu\nu}R = -\kappa T_{\mu\nu}, \quad . \quad . \quad . \quad (9.5)$$

where  $\kappa$  is a constant, and

$$R_{\mu\nu} = B_{\mu\nu}^{\sigma},$$

$$R = g^{\mu\nu}R_{\mu\nu},$$

the tensor  $B$  being the curvature tensor. We first write the equations (2.3) in the form

$$\frac{\partial g_{\mu\nu}}{\partial x^{\alpha}} = g_{\sigma\nu}\Gamma_{\mu\alpha}^{\sigma} + g_{\mu\sigma}\Gamma_{\nu\alpha}^{\sigma}. \quad . \quad . \quad . \quad (9.6)$$

If we transform these equations to a normal coordinate system, differentiate, and evaluate at the origin of the

\* A. Einstein, "Ueber Gravitationswellen," *Berlin Sitzungsberichte*, p. 154 (1918).

normal coordinates, we obtain

$$g_{\mu\nu, \alpha\beta} = g_{\sigma\nu} A_{\mu\alpha\beta}^{\sigma} + g_{\mu\sigma} A_{\nu\alpha\beta}^{\sigma}, \quad \dots \quad (9.7)$$

where  $g_{\mu\nu, \alpha\beta}$  is the second extension of the fundamental metric tensor  $g_{\mu\nu}$ , and the  $A$ 's are normal tensors. Now the normal tensor  $A_{\mu\alpha\beta}^{\sigma}$  and the curvature tensor  $B_{\mu\alpha\beta}^{\sigma}$  satisfy the equations

$$3A_{\mu\alpha\beta}^{\sigma} = B_{\mu\alpha\beta}^{\sigma} + B_{\alpha\mu\beta}^{\sigma} \quad \dots \quad (9.8)$$

identically. Using this identity, we may show that

$$3g_{\mu\nu, \alpha\beta} = g_{\alpha\sigma} (B_{\mu\beta\nu}^{\sigma} + B_{\nu\beta\mu}^{\sigma}). \quad \dots \quad (9.9)$$

Hence \*

$$\square g_{\mu\nu} = \frac{2}{3} R_{\mu\nu}. \quad \dots \quad (9.10)$$

By means of the identity (9.10) we easily transform the equations (9.4) into the Einstein equations (9.5). Hence the equations (9.4) contain the conservation equations (8.2), since it is well known that the divergence of the left member of (9.5) vanishes identically.

### 10. Motion of a Mass Particle.

The differential equations of motion of a freely-moving mass particle in the special theory of relativity are

$$\frac{d^2 y^i}{ds^2} = 0, \quad \dots \quad (10.1)$$

where  $y^0$  denotes the time and  $(y^1, y^2, y^3)$  are the coordinates of a rectangular coordinate system. These equations, when referred to the origin of the point-inertial system, are the differential equations of a path (2.1). Hence, according to the principle of equivalence, the track of a freely-moving mass particle in the general theory of relativity is a path (2.1). The equations of motion of the freely-moving mass particle which pass through the origin of the point-inertial system will therefore be

$$y^i = \xi^i s, \quad \dots \quad (10.2)$$

where the  $\xi$ 's are constants. Hence to the observer at the origin of the point-inertial system the particle will appear to move in a euclidean straight line. But the particle will not in general appear to move in a euclidean straight line if it does not pass through the origin of the point-inertial system.

\* The second extension  $g_{\mu\nu, \alpha\beta}$  is identical with a tensor  $\phi_{\mu\nu, \alpha\beta}$  defined by Birkhoff, who also obtains equations which are essentially the same as (9.10). Cf. G. N. Birkhoff, *loc. cit.* pp. 123 and 229.

11. *Track of a Light Ray.*

In the special theory of relativity the track of a light ray satisfies the differential equations (10.1) and also the condition that along it the constant  $\mu=0$ . Hence, according to the principle of equivalence, the track of a light ray in the general theory of relativity is a path (2.1) of zero length. As in the case of the mass particle, the observer at the origin of the point-inertial system will consider the track of the light ray which passes through the origin to be a euclidean straight line; but in general this will not be the case if the track does not pass through the origin.

A path (2.1) is uniquely determined by a set of initial conditions (3.1) and (3.2). Hence, if we assume that the track of a light ray is a path (2.1), it should be possible to determine this path by imposing the initial condition that at a remote point where the metric may be assumed to be galilean the ray has the velocity of light  $c$  in the ordinary sense, *i. e.*

$$\left(\frac{dx^1}{dx^0}\right)^2 + \left(\frac{dx^2}{dx^0}\right)^2 + \left(\frac{dx^3}{dx^0}\right)^2 = c^2, \quad . \quad . \quad . \quad (11.1)$$

where  $x_0$  denotes the time and  $(x^1, x^2, x^3)$  are rectangular coordinates.

The problem of showing that such a determination of the light path would be identical with the determination given by the condition that the path be of zero length was proposed to me by Professor Swann. The solution of this problem is immediate, for if we introduce the parameter  $s$  in (11.1) this equation becomes

$$c^2 \left(\frac{dx^0}{ds}\right)^2 - \left(\frac{dx^1}{ds}\right)^2 - \left(\frac{dx^2}{ds}\right)^2 - \left(\frac{dx^3}{ds}\right)^2 = 0 \quad . \quad (11.2)$$

or

$$g_{\alpha\beta} \frac{dx^\alpha}{ds} \frac{dx^\beta}{ds} = 0, \quad . \quad . \quad . \quad . \quad (11.3)$$

where the  $g$ 's have galilean values. But (11.3) must be satisfied at all points of the light path, since it is satisfied initially. Hence  $\mu=0$  for the light path, and the path is of zero length. Conversely, if the light track is a path of zero length and the  $g$ 's may be assumed to have galilean values at some remote point, then the ray has the velocity of light  $c$  in the galilean sense at this point.

We should notice that in the solution of this problem we have made explicit use of the condition  $\mu=0$  for a path of zero length.

GIII. *An Effect of Argon on the First Positive Band Spectrum of Nitrogen.* By R. C. JOHNSON, B.A., Ph.D., Lecturer in Physics, Queen's University, Belfast \*.

[Plate XXVI.]

THE first positive band spectrum of Nitrogen is peculiar in the extent to which it may be modified under various conditions of excitation. It was shown in 1911 by Strutt and Fowler † that one such modification of the system constituted part of the spectrum of the nitrogen afterglow. This consisted in a special development of some three of the more refrangible flutings in each band group, or, more precisely, the luminous energy was found to be concentrated in three only of the thirteen series which normally express the complete radiation of the system. Thus, the series developed are obtained by putting

$$\left\{ \begin{array}{ll} m = 47 & \text{and } p = 42, 43, 44, \\ m = 46 & \text{and } p = 41, 42, 43, 44, \\ m = 45 & \text{and } p = 40, 41, 42, 43, \end{array} \right.$$

in

$$\nu = 22785 \cdot 1 - \frac{30 \cdot 319}{8} (2m)^2 + \frac{29 \cdot 363}{8} (2p + 1)^2.$$

Further modification of the system has been described by Rayleigh ‡, when the afterglow is produced from mixtures of nitrogen with the inert gases helium, argon, and neon. The most remarkable feature (which was studied in some detail in the case of helium) is a pronounced shift of spectral intensity towards the less refrangible end as the percentage of the inert gas in the mixture is increased. Under these circumstances the selective action of the afterglow conditions, together with the energy displacement induced by the inert gas, render the first positive band spectrum of nitrogen almost unrecognizable. СВЕТЛОТ

More recently, variations induced by the inert gases in the fine structure of the second positive bands of nitrogen have been described by Steubing and Toussaint §, but no mention is made by them of similar variations in the first positive bands.

While working with tubes containing argon imperfectly

\* Communicated by Prof. W. B. Morton, M.A.

† Proc. Roy. Soc. A, lxxxv. p. 377 (1911), and later papers.

‡ Proc. Roy. Soc. A, cii. p. 453 (1923).

§ *Zeitschr. f. Phys.* Jan. 1924, p. 128.

purified—*i.e.*, mixed with a trace of nitrogen—we have noticed the appearance of the band spectrum in a considerably modified form. The effect is similar to that in the afterglow, and consists in the development of a few only of the band heads of each group. The selection is most pronounced with a trace of nitrogen in high-pressure argon. With increasing percentage of nitrogen the selection of bands which become visible increases almost symmetrically, the normal development of the spectrum being restored for percentages greater than about five.

This selective action of argon on the first positive band spectrum, though similar in character, is to be distinguished in origin from the selective effect found in the nitrogen afterglow. In the experimental work, we used wide-bore glass discharge-tubes containing the mixed gases at a total pressure of 10 mm. and excited by an ordinary uncondensed discharge. Under these circumstances the afterglow was not visible unless the percentage of nitrogen was considerable (say greater than 20). Even if it be suggested that at lower percentages the nitrogen afterglow might have been present though not sufficiently intense for visual observation, it is clear that this could not account for an effect which is *most* pronounced with the *lowest* percentages of nitrogen (when the supposed afterglow would be least strong). Further, Rayleigh\* observed that in the production of the afterglow (using a *condensed* discharge) in mixtures of nitrogen and argon, the glow became too faint for observation for percentages of nitrogen less than 25.

These facts finally dispose of any possibility of an afterglow origin for the selective effect which we have described.

The modified band spectrum has been further investigated by us, and a systematic search was made for an induced energy displacement in the several band groups. A series of tubes containing variously accurately known percentage mixtures of nitrogen and argon were photographed through a neutral wedge† mounted in front of the slit of a prism spectroscope. In this way negatives were obtained showing the intensity distribution in the band system. Pl. XXVI. shows a few typical photographs. Spectra 4 and 5 are respectively of pure nitrogen

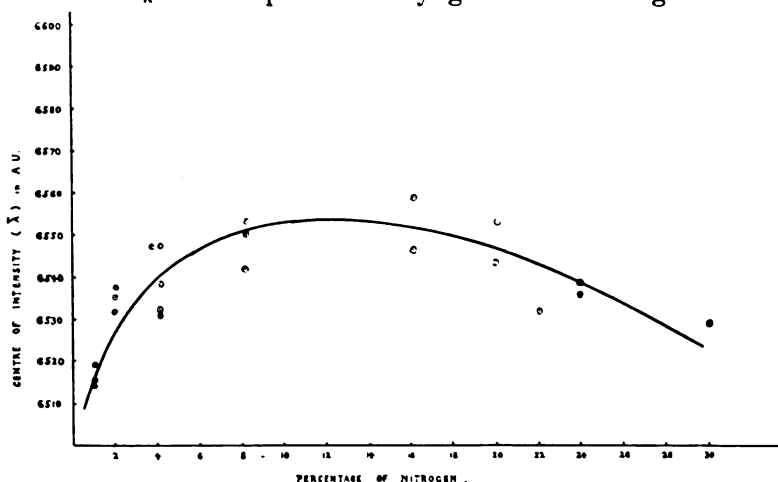
\* *Loc. cit.*

† For the theory of the neutral wedge, see papers by Merton and Nicholson: *Phil. Trans. A*, cexvi. p. 459, and cexvii. p. 239.

at low pressure, and of a trace of nitrogen in 10 mm. of argon. The latter shows the selective effect strongly. Spectra 1 and 2 are, from this point of view, over-exposed. By successive photographic reproduction of the negatives, plates were obtained having sufficiently sharp contrast to permit of micrometric measurement. The height of the band heads in each group was measured, and these were converted into photographic intensities by the formula

$$I = \log_{10}^{-1}(d_{\lambda}h),$$

where  $d_{\lambda}$  is the optical density gradient of the gradient



of the wedge for a wave-length  $\lambda$ , and  $h$  is the height of the band head. By forming the quantity

$$\bar{\lambda} = \frac{\sum I\lambda}{\sum I}$$

for each band group, we obtain a wave-length which may be described as the "optical centre of gravity," or, better, the "centre of intensity" of the group. Attention was confined to the red group, and the large quantity of data accumulated is disposed in the graph of "Centre of Intensity" against "Percentage of Nitrogen." It will be observed that the range of experimental error seems rather wide. This, however, is difficult to avoid, as it arises from

- (1) Errors in  $\lambda$  due to inaccuracy in measurement of  $h$ , owing to irradiation etc., and
- (2) Variation from the initial percentage due to appreciable disappearance of nitrogen in the discharge.



The results, however, are sufficient to indicate that for traces of nitrogen in argon there is an energy displacement of some 30 to 40 Å.U. towards the more refrangible end. This, indeed, is the analogue of the selection of three of the *more refrangible* flutings of the red group in the afterglow spectrum. Both phenomena are illustrated in the graph, the downward course of the curve for higher percentages being interpreted as due to the appreciable formation of active nitrogen.

#### DISCUSSION.

According to Fowler and Strutt\*, the afterglow is produced during the re-formation of molecular nitrogen from atomic or so-called "active" nitrogen. The electrical conditions within the afterglow must therefore be the result of the inter-atomic electric fields. In the enlarged state of the activated molecules these fields naturally have effects on neighbouring or interposed atoms and molecules of another kind, which will as a consequence have their spectra excited. In this connexion an application of Klein and Rosseland's theory of inelastic collisions of the second type has recently been made by Saha and Sur†. They have shown that the excitation of other spectra in the afterglow is in every case explained by a "radiationless transfer" of energy from the active nitrogen molecules to the particular molecules introduced. This may take place to the extent of the total energy with which the activated molecules are loaded, viz. about 8.5 volts. No attempt, however, is made by these investigators to explain that peculiar selection of the first positive bands of nitrogen which constitute the visible spectrum of the afterglow. It seems at first sight attractive to assume that it originates in radiationless transfer from the activated to the inactive molecules, which latter must be present in large excess. As a consequence we should expect initial nuclear orbits of small quantum number to preponderate. Taking the red band group, by way of illustration, we find, for example‡, the transitions giving the afterglow are from initial quantum orbits  $p=40, 41, 42$  to final orbits  $m=45, 46, 47$ ; while  $p=43, 44, 45$ , and 46, which usually occur strongly in the first positive band system, are absent. On the other hand, orbits  $p=38$  and 39, which usually occur faintly, are not present at all in the afterglow, while the above theory suggests that they would be strengthened.

\* *Loc. cit.*

† *Phil. Mag.* (6) xlviii. p. 421 (1924).

‡ See table in *Phil. Mag.* (6) iii. p. 348 (1902).

We now proceed to discuss the consequences of the experimental work described in the present paper.

The effect of argon which we have described would seem to be quite in harmony with the view advanced tentatively elsewhere\*, that the electrical conditions obtaining in the afterglow are of a similar character to those found when an uncondensed discharge is passed through high pressure argon. It is reasonable to assume that at any given time the activated molecules will only constitute a very small fraction of the total number, so that the greater part will be ordinary nitrogen molecules, and in this inactive state must bear the relation of a comparatively high-pressure inert gas towards those which are radiating. The similarity which experiment appears to suggest is therefore between molecules radiating, on the one hand, in a virtually inert atmosphere (of un-ionized nitrogen molecules) where only inter-atomic fields due to the activated molecules exist, and, on the other hand, in an inert atmosphere of a foreign gas to which external electric fields are applied. It may be reasonably contended that under *ordinary discharge conditions* the radiating molecules will only constitute a very small fraction of the total number present, which suggests at first sight that the above similarity should hold in every case. The fundamental difference, however, between ordinary discharge conditions and those of the afterglow is that in the former external electric fields are applied, while in the latter case there are no fields except such as might arise from the activated molecules themselves. In the afterglow the excess of un-ionized molecules breaks up any fields that might exist between the activated ones, so that the latter radiate in the more or less complete absence of electrical fields. This we believe to be the clue to the structure of the afterglow spectrum. In high-pressure argon we probably have an approximation to these conditions. Here, in order to produce the radiation, an external field is applied; but the excess of argon atoms, which themselves produce no radiation and are therefore closed systems, operate so as to break up strong electric fields, in this way shielding the radiating nitrogen molecules from all those which are other than of the mildest character.

From this point of view the afterglow selection might be regarded as the "normal" radiation of this molecule, and the more familiar first positive band spectrum a result of the influence of electrical fields on the radiation. This does not furnish by any means a complete explanation, but as a working hypothesis it explains the similarity which

\* Proc. Roy. Soc. A, cvi. p. 200 (1924).

experiment has indicated, and it may be of service in elucidating the reasons for structural modifications induced in spectra excited in the afterglow. It would follow from the analogy that, just as the selective action on the nitrogen bands is most pronounced with only a trace of nitrogen present in argon, so the afterglow selection should be most pronounced the instant before the glow dies away—that is to say, the light from an end-on stream of nitrogen in which the afterglow is dying away would yield an intensity distribution which is but the integral of a varying one. According to our theory, this distribution is a function of the percentage of active molecules present, so that the range of the integration would be from this initial value to zero. A critical test would therefore be found in a comparison of the intensity distribution in the first positive bands photographed in the afterglow at various points down the stream. (These would require, of course, very different times of exposure.)

It seems quite possible that all the various modifications produced in spectra excited by the nitrogen afterglow may be reproduced in high-pressure argon, and this matter is also receiving further investigation.

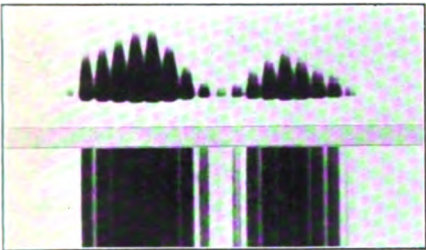
I wish to take the opportunity of thanking Mr. W. H. B. Cameron and Miss M. E. Hall for their valuable assistance.

#### *Abstract.*

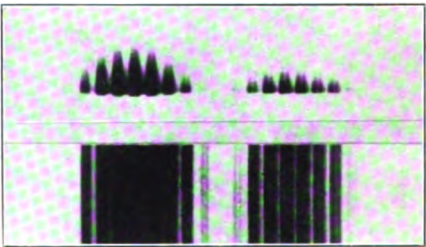
Traces of nitrogen in high-pressure argon show the first positive band spectrum in a considerably modified form. This consists in a selection of a few only of the band heads of the various groups, and the general effect is similar to that found in the afterglow spectrum. Quantitative investigations are described which indicate that there is an energy displacement towards the more refrangible end of each band group. This also is similar to the conditions of the afterglow. It is suggested that all the phenomena hitherto regarded as peculiar to the electrical conditions obtaining in the afterglow may be reproduced in high-pressure argon. The bearing of these facts on the nature of the afterglow spectrum is discussed.

#### DESCRIPTION OF PLATE XXVI.

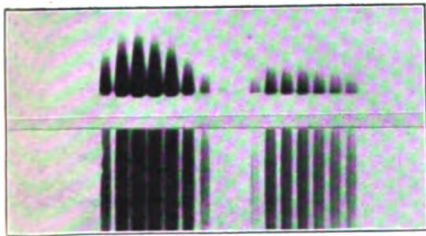
- No. 1. Spectrum and wedge photograph of argon-nitrogen mixture containing less than 1 per cent. of nitrogen.
- No. 2. Argon-nitrogen mixture containing 2 per cent. nitrogen.
- No. 3. Argon-nitrogen mixture containing 12 per cent. nitrogen.
- No. 4. Pure nitrogen at low pressure. Wide-bore tube. Uncondensed discharge.
- No. 5. Spectrum photograph showing the selective effect of argon on the nitrogen band spectrum. Taken from a tube containing a trace of nitrogen in argon at 10 mm. pressure.



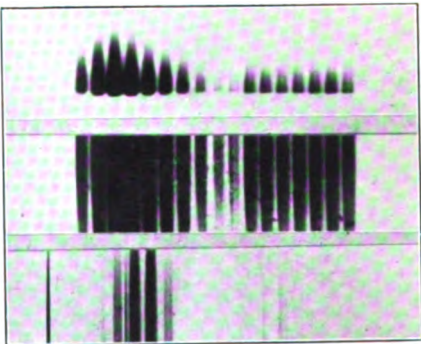
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CIV. *The Decay of Radium E.*

By L. BASTINGS, B.A., M.Sc. (N.Z.) \*.

## INTRODUCTION.

THE  $\beta$ -ray emission of radium E has long been of considerable interest. Schmidt† first showed that the  $\beta$  rays are resolved in a transverse magnetic field into a continuous spectrum, in which have since been detected no spectral lines such as are produced with all other  $\beta$ -ray bodies except UrX. This spectrum from RaE indicates a continuous distribution of velocity in the rays emitted, from very small velocities up to, according to Danysz‡, velocities in the neighbourhood of  $2.8 \times 10^{-10}$  cm. per sec. At the same time, the amount of  $\gamma$  radiation is extremely small, its ionizing power having been variously estimated by Schmidt§ and by Meyer and Schweidler|| at from .016 to .033 per cent. of that due to the  $\beta$  rays. This small ratio is in marked contrast to that for all other  $\beta$ -ray substances: *e.g.*, for RaC the ratio is approximately 100 per cent., for ThD 74 per cent., and even for UrX 2 per cent.

It is now generally considered probable that the  $\beta$  rays comprising a line-spectrum are ejected from extranuclear orbits by the action of  $\gamma$  rays proceeding from the nucleus, and owe their varied velocities to their originating from different energy-levels of the atom. But in the case of RaE, as with other continuous  $\beta$ -ray spectra, all the  $\beta$  rays probably have their origin in the nucleus itself, and it is not easy to see how such great differences in velocity can arise in the disintegration of nuclei presumably all alike. Now, one important respect in which the atoms are assumed to be alike is implied in the exponential law of decay—viz., that all the atoms present have the same probability of decay, irrespective of any attendant circumstances. But a conceivable explanation of the heterogeneity of the rays might be found in the assumption that the atoms do not all possess exactly the same probability of decay; that, for example, the atoms evolving fast  $\beta$  rays might disintegrate at a more rapid rate than those ejecting slow particles, and in consequence possess a decay constant differing from the average constant, as deduced from the usual decay measurements. Now the faster  $\beta$  particles can easily be separated from the rest by interposing a

\* Communicated by Sir E. Rutherford, F.R.S.

† *Phys. Zeit.* viii. p. 361 (1907).‡ *Le Radium*, x. p. 4 (1913).§ *Wien. Ber.* cxv. p. 119 (1906).§ *Loc. cit.*

suitable thickness of metal foil; and if there is any difference in the average life of the atoms in the way suggested, the ionization produced by the faster particles should die away more rapidly than that revealed by the heterogeneous beam from the bare source. Such a theory of the continuous spectra can best be tested by means of RaE, since the problem is not complicated by the presence of any homogeneous  $\beta$  rays, or any appreciable  $\gamma$  radiation.

Further interest is added to the case of RaE by the fact that widely differing values of the half-period have been obtained, while at one time it was even believed by some that RaE consisted of two distinct bodies of periods as widely apart as 4.8 and 6.2 days. The following is a summary of the results on record for the half-period:—

Rutherford	.....	(1)	4.5 days
"	.....	(2)	6 "
Giesel	.....	(3)	6 "
Meyer & Schweidler	(4)	4.8 & 6.2	"
Antonoff	.....	(5)	5 "
Thaller	.....	(6)	4.85 "

(1) Phil. Trans. A, cciv, p. 169 (1905); Phil. Mag. viii, p. 636 (1904).

(2) Phil. Mag. x, p. 290 (1905).

(3) Ber. d. D. Chem. Ges. xxxix, p. 780 (1906).

(4) Wien. Ber. cxvi, p. 701 (1907).

(5) Phil. Mag. xix, p. 825 (1910).

(6) Wien. Ber. cxxi, p. 1611 (1912).

#### EXPERIMENTAL PROCEDURE.

The RaE sources were prepared by dissolving in dilute HCl the equilibrium products contained in old emanation tubes, and electrolyzing out the E on to platinum electrodes with a current density of about  $2 \times 10^{-4}$  amps. per sq. cm. The deposit was then dissolved off in dilute HCl, and a clean nickel disk rotated in the warm solution for from a half to two hours. With some of the smaller sources, the electrolytic process was omitted. This procedure resulted in fairly pure RaE, the amount of RaD obtained producing a residual activity which in only one case exceeded  $\frac{1}{2}$  per cent. of the initial activity of the source, and in most cases was considerably less than this. (The percentage residues for the various sources were: .08, .03, .14, .002, .61, .22, .05, .008.) In every case these residual effects were carefully measured some weeks afterwards, and due allowance made by subtracting the value for the residue from the values obtained throughout the decay.

Comparison was made between a bare source of weak intensity and a stronger source covered with a suitable

thickness of aluminium, up to 1.1 mm., in which case the intensity of the ionization is reduced to less than 1 per cent. of its original value. Also both sources were deposited on equal-sized disks of the same metal, this precaution being perhaps of importance in view of the evidence recently adduced by Mlle St. Maracineanu\* of the slow diffusion of radioactive sources into metals on which they are deposited.

Three different methods of attacking the problem were successively attempted :—

(a) A direct estimate of the apparent decay constant of the sources was made by measuring the ionization produced by each, at regular intervals, for a period of up to 20 days. The measurements were made in the usual way with a  $\beta$  ray electroscope, with the leaf insulated by a sulphur bead inside the ionization chamber. The electroscope was standardized regularly with a constant  $\beta$ -ray source—viz., an old emanation tube in equilibrium, in which the controlling factor RaD, having a half-period of about 17 years, would vary by only 0.23 per cent. in 20 days. The constancy of the natural leak was checked at frequent intervals.

Further reference will be made to these measurements later. They revealed no difference of the kind sought to an accuracy of 1 per cent.

(b) In the next method, two sources were initially adjusted as before to give identical ionization at the same instant, and an attempt was made to measure any subsequent possible difference in the ionization produced by them. Two exactly similar ionization cans were constructed, and their insulated electrodes connected together to one pair of quadrants of a Dolezalek electrometer, used heterostatically. The walls of the ionization chambers were connected to a suitable high voltage, one being maintained positive and the other negative. Any initial difference, such as that due to unequal natural leak, was taken up by a subsidiary ionization can of smaller dimensions, suitably arranged. The decay of the sources was followed for about 20 days; but a limit to the accuracy was imposed by the large capacity of the system in relation to the comparatively small sources available. No further information on the problem was added to that obtained in (a); and the method proved more difficult and less reliable.

(c) A third method proved much more successful. The sources, adjusted to approximate equality, as before, were measured alternately by the  $\beta$ -ray electroscope of method (a). By making a large number of comparisons at frequent

\* C. R. clxxvii. p. 1215 (1923).



purified—*i. e.*, mixed with a trace of nitrogen—we have noticed the appearance of the band spectrum in a considerably modified form. The effect is similar to that in the afterglow, and consists in the development of a few only of the band heads of each group. The selection is most pronounced with a trace of nitrogen in high-pressure argon. With increasing percentage of nitrogen the selection of bands which become visible increases almost symmetrically, the normal development of the spectrum being restored for percentages greater than about five.

This selective action of argon on the first positive band spectrum, though similar in character, is to be distinguished in origin from the selective effect found in the nitrogen afterglow. In the experimental work, we used wide-bore glass discharge-tubes containing the mixed gases at a total pressure of 10 mm. and excited by an ordinary uncondensed discharge. Under these circumstances the afterglow was not visible unless the percentage of nitrogen was considerable (say greater than 20). Even if it be suggested that at lower percentages the nitrogen afterglow might have been present though not sufficiently intense for visual observation, it is clear that this could not account for an effect which is *most* pronounced with the *lowest* percentages of nitrogen (when the supposed afterglow would be least strong). Further, Rayleigh\* observed that in the production of the afterglow (using a *condensed* discharge) in mixtures of nitrogen and argon, the glow became too faint for observation for percentages of nitrogen less than 25.

These facts finally dispose of any possibility of an afterglow origin for the selective effect which we have described.

The modified band spectrum has been further investigated by us, and a systematic search was made for an induced energy displacement in the several band groups. A series of tubes containing variously accurately known percentage mixtures of nitrogen and argon were photographed through a neutral wedge† mounted in front of the slit of a prism spectroscope. In this way negatives were obtained showing the intensity distribution in the band system. Pl. XXVI. shows a few typical photographs. Spectra 4 and 5 are respectively of pure nitrogen

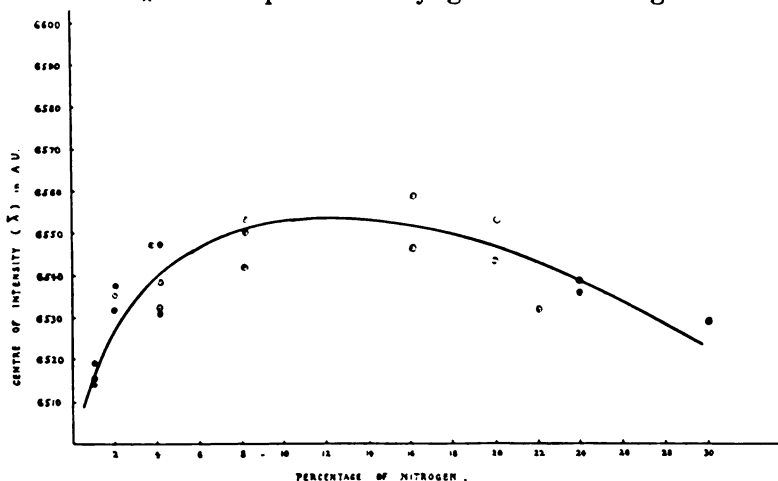
\* *Loc. cit.*

† For the theory of the neutral wedge, see papers by Merton and Nicholson: Phil. Trans. A, cexvi. p. 459, and cexvii. p. 239.

at low pressure, and of a trace of nitrogen in 10 mm. of argon. The latter shows the selective effect strongly. Spectra 1 and 2 are, from this point of view, over-exposed. By successive photographic reproduction of the negatives, plates were obtained having sufficiently sharp contrast to permit of micrometric measurement. The height of the band heads in each group was measured, and these were converted into photographic intensities by the formula

$$I = \log_{10}^{-1}(d_{\lambda}h),$$

where  $d_{\lambda}$  is the optical density gradient of the gradient



of the wedge for a wave-length  $\lambda$ , and  $h$  is the height of the band head. By forming the quantity

$$\bar{\lambda} = \frac{\sum I\lambda}{\sum I}$$

for each band group, we obtain a wave-length which may be described as the "optical centre of gravity," or, better, the "centre of intensity" of the group. Attention was confined to the red group, and the large quantity of data accumulated is disposed in the graph of "Centre of Intensity" against "Percentage of Nitrogen." It will be observed that the range of experimental error seems rather wide. This, however, is difficult to avoid, as it arises from

- (1) Errors in  $\bar{\lambda}$  due to inaccuracy in measurement of  $h$ , owing to irradiation etc., and
- (2) Variation from the initial percentage due to appreciable disappearance of nitrogen in the discharge.

intervals over a period of several hours, and discarding all but highly concordant results (due allowance being made for decay), values can be obtained for the ratio between the sources, from which have been eliminated any sensible errors due to variations in the action of the electroscop. Such average ratios were obtained at least twice daily for about three weeks.

### RESULTS.

The results of this last method are best revealed by tabulating, in their order, the ratios obtained, the values in each column corresponding to measurements spread over five consecutive days.

	1·138	1·137	1·140	1·144
	1·140	1·134	1·143	1·144
	1·144	1·140	1·144	1·139
	1·137	1·141	1·145	1·140
	1·136	1·137	1·143	1·145
	1·142	1·138	1·139	1·135
	1·139	1·144	1·143	1·139
	1·139	1·141	1·136	1·136
	1·146	1·137	1·139	1·135
	1·134	1·141	1·139	1·137
				1·141
Means .....	1·139 <sub>5</sub>	1·139 <sub>0</sub>	1·141 <sub>1</sub>	1·139 <sub>6</sub>
Average .....	1·139 <sub>6</sub>			
Mean deviation } from average .	·002 <sub>8</sub>	·002 <sub>4</sub>	·002 <sub>6</sub>	·003 <sub>0</sub>
Maximum deviation from average .....				·006 <sub>1</sub>
Mean ..	..	..	.....	·002 <sub>7</sub>

A real change in the ratio from 1·139 to 1·141 in 5 days would correspond to a difference in decay constant of 0·3 per cent. between those atoms evolving fast particles and the average atom. These results therefore point conclusively to the absence of any systematic difference in the average life of the two classes of atoms. We are therefore still without any adequate explanation of the homogeneity of the  $\beta$  rays in the continuous spectrum of this or other  $\beta$ -ray products.

It may also be remarked that the above results indicate that a  $\beta$ -ray electroscop, when used under the most favourable circumstances, may be relied on to about 1 in 500.

### THE DECAY CONSTANT.

The value for the half-period usually accepted is 4·85 days, as deduced by Thaller \* by averaging 16 results (varying from 4·6 to 5·0) of measurements made by him in the usual way.

In connexion with the measurements of this constant undertaken under method (a) above, it was soon realized

\* *Wien. Ber.* cxxi. p. 1611 (1912).

that Thaller's value is too low. So further measurements of the constant were made with several fresh sources in the manner previously indicated. In all, seven sources have been followed for from 20 to 30 days; and in every case the residual activity, due to RaD contamination, has been estimated after 50 days or more, and due correction applied. The most probable value of the constant in each case, and its probable error, were deduced from the data by the method of least squares; while to the various values of the activity of each source, weights were attached, varying in magnitude with the activity of the source. The average result was also arrived at by attaching weights in accordance with the above probable errors.

The results are summarized in the accompanying table.

Source.	Period, in days.	Probable error.	Weight attached.
A .....	5.04	$\pm .04$	1
B .....	4.96	$\pm .03$	1
C .....	5.02	$\pm .04$	1
D .....	5.02	$\pm .02$	2
E .....	4.98	$\pm .02$	2
F .....	4.97	$\pm .01$	3
G .....	4.96	$\pm .01$	3
Weighted mean..... $t = 4.98$ , days $\pm .00_4$			
Corresponding decay constant... $\lambda = 0.139_6$ day $^{-1}$			

### Table of Decay.

As this constant differs by about 3 per cent. from that adopted for tables of decay published for RaE\*, it may be

Hours.	Activity.	Days.	Activity.	Days.	Activity.
0	1.0000	0	1.0000	17	.0941
0.5	.9971	1	.8704	18	.0819
1	.9942	2	.7572	19	.0713
2	.9885	3	.6592	20	.0620
3	.9827	4	.5734	25	.0310
4	.9771	5	.4990	30	.0155
5	.9714	6	.4343	35	.0077
6	.9658	7	.3780	40	.0038
7	.9602	8	.3290	45	.0019
8	.9542	9	.2862	50	.0010
9	.9491	10	.2491	60	.0002
10	.9436	11	.2168	66	.0001
11	.9381	12	.1886		
12	.9328	13	.1642		
15	.9168	14	.1426		
18	.9011	15	.1243		
21	.8854	16	.1082		

\* E. g. Meyer and Schweidler, *Radioaktivitat*, 1916, p. 365.

of value to add such a table, based on the above value of the constant, and calculated by the aid of Newman's Table of Exponentials\*.

## SUMMARY.

(1) No appreciable difference has been detected between the decay constant of those radium E atoms ejecting fast  $\beta$  particles and the average radium E atom.

(2) A value of the decay constant of radium E,

$$\lambda = 0.139_0 \pm .000_1 \text{ day}^{-1},$$

has been obtained, corresponding to a half-period of 4.98<sub>5</sub> days.

I have much pleasure in recording my gratitude to Professor Sir Ernest Rutherford for suggesting the problem, and for his helpful interest during its prosecution; also to Dr. J. Chadwick for criticism and help, especially in the preparation of the unusually large RaE sources required.

The Cavendish Laboratory,  
Cambridge,  
July 28, 1924.

*C.V. The Apparent Value of Poisson's Ratio for Beams of Varying Cross-Section. By H. WRIGHT BAKER, M.Sc., A.M.I.M.E., Lecturer in Engineering at the University of Manchester†.*

**W**HEN a beam is subjected to a uniform bending moment, curvature occurs in a plane containing the longitudinal axis of the beam and also in transverse planes perpendicular to this axis. Assuming the simple theory of bending to be applicable, it can be shown that the ratio of the two radii of curvature has the same value as Poisson's ratio for the material of the beam. Early experimental determinations of Poisson's ratio for metals by the method of flexures were made by Mallock (Proc. Roy. Soc. xxix. 1879). Four small wire pillars were attached to the surface of the beam, in the planes of bending, so that on loading the beam the free ends of a pair of pillars either approached each other or receded according to the direction of curvature. By measuring these relative movements with the aid of a microscope, and knowing the length of the pillars and the distance apart of their bases, the radii of curvature of the beam were found.

\* Trans. Camb. Phil. Soc. xiii. p. 145 (1883).

† Communicated by the Author.

The method was further improved by Carrington (Phil. Mag. [6] xli. p. 206, 1921), who fastened small mirrors to the pillars and determined their relative angular movements by measuring the deflexions produced on beams of light after successive reflexion from the two mirrors of each pair.

Guided by the sensitiveness of the methods of measurement employed, these investigators have used beams capable of considerable flexure, the breadth:depth ratio chosen being 4 and 5.7. Experiments by the author, while approximately confirming the results for thin beams obtained by Carrington, lead him to doubt the constancy of the values for a given material but with varying cross-sections. Tests have therefore been made on a series of beams for which the ratio of breadth to depth varied from 3.7 to 0.27.

When experimenting on narrow beams, the small deflexions and the shortness of the base available for the measurement of anticlastic curvature prevent the use of Carrington's method in its simple form and without the employment of elaborate means of preventing vibration.

The system of measurement to be described virtually consists in replacing Carrington's mirrors by pieces of plate glass, adjusting these to be approximately parallel and almost in contact, and measuring the spacing, perpendicular to the beam, of the interference bands seen when monochromatic light is reflected from the two inner surfaces.

If the plates are secured to the sides of a beam of breadth " $b$ ," and " $n$ " is the change, produced by bending, in the number of bands between two gauge lines at a distance " $l$ " apart, then " $\theta$ ," the angle of inclination of the sides of the beam, is given by  $n \times \frac{1}{2}$  (wave-length of light)/ $l$ , and the corresponding radius of anticlastic curvature is  $b/\theta$ .

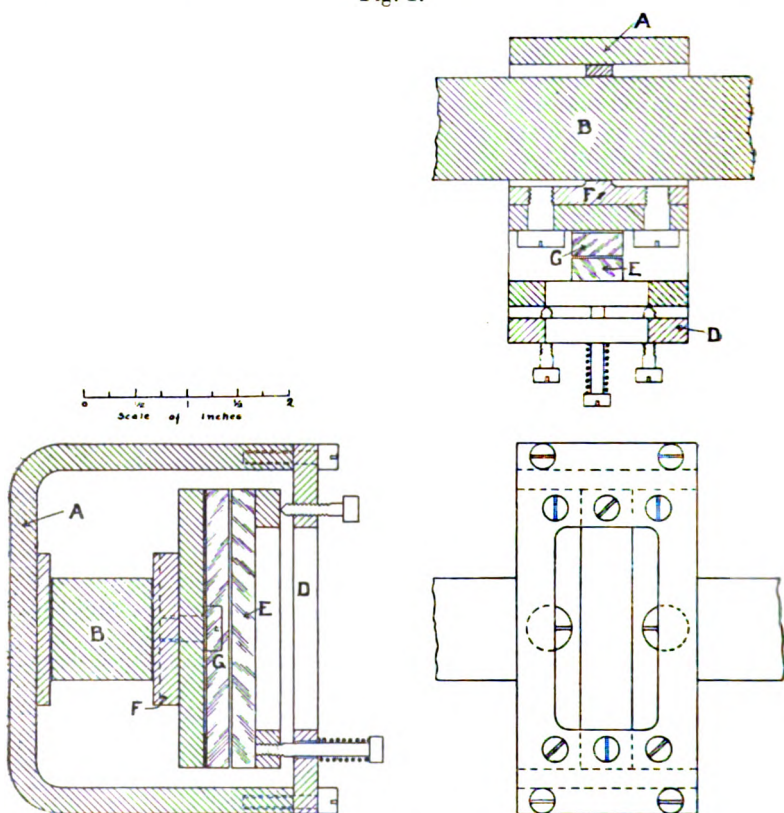
The glass plates, carried in adjustable brass frames, were at first clamped to the beam, but persistent "creep" occurred during the tests, both when using plane and 3-point contacts. A number of other methods have been tried, the most satisfactory being that of soldering the frames to the beam, using a solder having a melting-point of about  $100^{\circ}$  C.

Fig. 1 shows the final form of the interferometer.

The body A is soldered to one side of the beam B, a packing strip a quarter of an inch wide being interposed. In the front-plate D a rectangular window is cut, and behind this, held on an adjustable frame, is a stout strip of plate-glass E. A brass back-plate F is soldered to the opposite side of the beam (the breadth of contact again being  $\frac{1}{4}$  in.), and carries the rear glass G. The rear reflecting surface is therefore controlled by the front side of the beam, and *vice versa*.

The chief advantages of this form of apparatus are its rigidity and ease of adjustment, and also the absence of any relative movement of the plates other than the angular movement to be measured, sharp definition of the interference bands being therefore maintained for all conditions of flexure. It is assumed that the sides of the beam, for a length of  $\frac{1}{4}$  in. where the interferometer is attached, remain

Fig. 1.



plane during bending, and that the glass plates are subjected therefore to the movement of the whole depth of the beam. Though "creep" has not been entirely eliminated, its magnitude has been reduced to reasonable dimensions, and further improvements might be effected by the provision of hardened and polished contacts on the adjusting mechanism.

The plates are illuminated from a distance of 2 feet by a sodium flame about 4 inches high, produced by hanging a fine strand of asbestos soaked with brine in a suitable

bunsen flame. Care is required to obtain a uniform light for all conditions of bending.

For counting the "bands" between two gauge marks drawn in ink on one of the reflecting faces, a low-power telescope is used. This is mounted on the horizontal axis of a theodolite frame to enable the image of the cross-hair to be traversed slowly across the field as a pointer, thus greatly reducing eye-strain.

In the tests recorded in the present paper the beams were supported on knife edges 21 inches apart, one of these having been free to swing horizontally to prevent end constraint. A state of pure bending was produced by loads applied outside the supports, these having been increased in stages to a maximum corresponding to a skin stress of 10,000 lb./in.<sup>2</sup> and then gradually reduced to zero. Longitudinal curvature was measured in the usual way with scale, mirror, and telescope, arranged on an optical base of 20 feet.

The tests cover the useful range of the interferometer for the deeper sections of beams, this being fixed almost entirely by the "creep." The change of zero-reading recorded has usually amounted to about one band, a comparatively small amount when dealing with shallow sections giving a total shift of 100 bands or more, but far outweighing all other sources of error for the deepest section used, for which a shift of only 11 bands was recorded. For very shallow sections a telescope of considerable power is required owing to the close spacing of the bands, and it is advisable to set the plates so that their relative inclination reverses at about half load. It has been customary to distribute the zero error equally between the curves of loading and unloading.

Preliminary tests on bright-rolled mild steel bars indicated a considerable variation in the apparent value of Poisson's ratio with change of section. The results, however, were not consistent, owing to a corresponding variation of the properties of the material due to rolling, affected to an unknown extent by the high temperature required to melt the tinsmith's solder which was then employed.

The curve shown in fig. 2 gives the results of 11 tests on "Armco" iron, the value obtained by Carrington for wrought iron being also added.

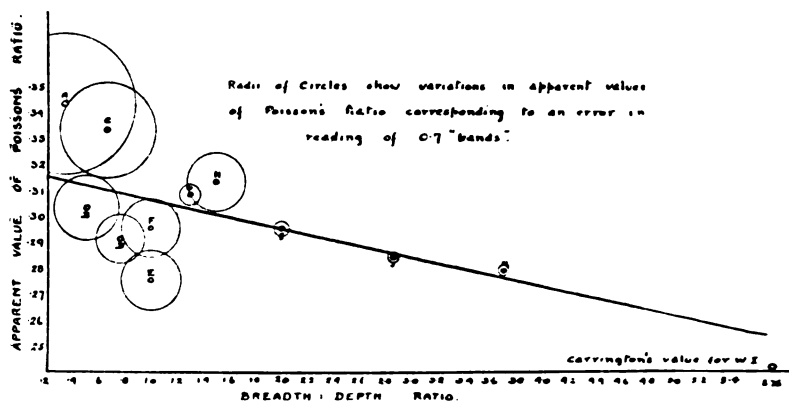
In addition to the distribution of the zero error as already indicated, small corrections have been made to the direct readings of longitudinal curvature. Within the limits of experimental error the radius of curvature has agreed with the simple theoretical value given by  $\frac{\text{moment of inertia of section}}{\text{bending moment}} \times E$ , where E is the modulus



of direct elasticity and is constant. The radius has therefore been re-calculated, assuming  $E$  to have the mean value obtained during the tests. In all cases the graphs of bending moment and radii of curvature have been straight lines.

With these corrections the greatest variation between the curve shown and the observation points is at E, and corresponds to an error of reading of two interference bands, the error at A and the mean error for the tests amounting to 0.8 band.

Fig. 2.



It would appear, therefore, that the apparent value of Poisson's ratio increases uniformly with the depth of section from about 0.26 for a breadth : depth ratio of 5.2 (Carrington's value .245 for a ratio of 5.7) to .315 for a ratio of 0.2, and is independent of the stress up to 10,000 lb./in.<sup>2</sup>

It is interesting to compare the variations shown by this curve for iron with the results obtained by Cornu (*Comptes Rendus*, 1869) and Straubel (*Annalen der Chemie und der Physik*, lxxiii. p. 395) for small glass beams, the radii of curvature in these cases being measured by placing a plate of glass on the upper surface of the beam and examining the interference bands shown by monochromatic light. The first observer records a variation from .227 for a breadth : depth ratio of 12 : 1 to a mean of .246 for a ratio of 2.7, the latter giving a corresponding variation over a more restricted range of beams.

In conclusion the author would acknowledge his indebtedness to Messrs. A. Markwick, B.Sc., and W. L. D. Martyn, B.Sc., for much valuable assistance in the experimental work.

CVI. *Latent Heats of Fusion*.—Part II. *Palmitic Acid and Benzene*. By Mrs. K. STRATTON, M.Sc., and Professor J. R. PARTINGTON, D.Sc.\*

THE experiments described in the present paper form a continuation of those previously published†, but the apparatus has been slightly modified for convenience in working.

### 1. PALMITIC ACID.

The Palmitic Acid used in the experiments was obtained originally from a specially pressed sample supplied by Price's Patent Candle Company. It was distilled twice at 100 mm. pressure, and the fraction coming over between 267° and 270° C. collected. This was recrystallized from petrol (B.Pt. 100°–110° C.); most of the acid was recrystallized at least twelve times.

After each recrystallization from petrol the product was dried in air, then put on a water-bath at 100°, and air drawn through it for about an hour to remove the last traces of petrol.

The recrystallizations were carried out with about ten different samples; the table below gives the results in two cases.

	1ST SAMPLE. Setting-Point.	2ND SAMPLE. Setting-Point.
6th recrystallization.....	62·125° C.	62·15° C.
7th       "       .....	62·185° C.	62·165° C.
8th       "       .....	62·215° C.	62·20° C.
9th       "       .....	62·215° C.	62·225° C.
10th       "       .....	62·245° C.	62·24° C.
11th       "       .....	62·25° C.	62·25° C.
12th       "       .....	62·25° C.	62·25° C.

The Setting-Point of the mixture of Samples I. and II. was 62·25° C.

The Melting-Point of the mixture of Samples I. and II. was 62·65° C.

The melting-point was taken in the following way:—Finely powdered acid was placed in a test tube supported in a 500-c.c. beaker containing 300 c.c. of water, fitted with an efficient stirrer, and the thermometer was used for the stirrer in the acid. The heating of the bath was very gradual: about 45 minutes were required to warm the water from 16° C. to the temperature of melting.

The setting-points of the acid referred to above were determined in the usual form of apparatus: an inner tube,

\* Communicated by the Authors.

† Phil. Mag. xliii. p. 436 (1922).

a strong test tube in this case, containing the powdered acid was supported by means of a cork in an air-jacket; the air-jacket was fixed in a water-bath, and the water in the bath heated and kept well stirred.

The acid in the inner tube was allowed to melt completely, then allowed to cool very slowly. As soon as the acid showed signs of setting, the bath was kept as nearly as possible at  $62.5^{\circ}\text{C}$ . with a very small flame and efficient stirring. The setting-point curves of pure specimens drawn from data of cooling experiments gave steady values at  $62.25^{\circ}\text{C}$ . The data previously recorded include the following :—

M.P. of Acid. Beilstein, vol. ii. p. 370:  $62.618^{\circ}\text{C}$ .  
Landolt-Börnstein, p. 374:  $62.618^{\circ}\text{C}$ .

S.P. of Acid. Landolt-Börnstein, p. 1430:  $60^{\circ}\text{C}$ .

Acid supplied by Kahlbaum, used in a previous research (Partington, Trans. Chem. Soc. xcix. p. 313, 1911), had a setting-point of  $60^{\circ}\text{C}$ .

The apparatus used in the previous experiments was modified to some extent. A stout cover for the whole apparatus, except for the inside beaker containing the acid, was made from sheet aluminium; the centre beaker was covered by a cork, as previously, cut so as to allow a space for the thermometer and heating-coil. The outermost enamelled iron vessel contained water at a temperature about  $2^{\circ}$  higher than that of the molten acid in the bath; the temperature of this water was kept fairly constant by placing the outer vessel in a large box packed with cotton-wool. The inside bath contained the pure acid in a molten condition and kept well stirred.

A weighed amount of the acid, well powdered, was placed in the innermost vessel, and the temperature gradually raised by being in contact with the bath of molten acid until a thermometer in the centre of it showed it to be at the setting-point  $62.25^{\circ}\text{C}$ . To ensure that the whole of the acid was at the setting-point, it was kept at this temperature for at least an hour before any heating by the coil was commenced.

The heating-coil in this case was of platinum wire joined to thick platinum leads. The wire was wound into a small coil of about  $\frac{3}{4}$  inch length, and the windings kept in position by being fixed on to a small piece of glass rod. The rod bearing the coil was fused on to about 6 inches of glass rod, and this longer rod could then be used as a stirrer during the experiment. For purposes of connexion, the thick platinum leads were soldered on to leads of thick copper wire.

The quantity of electricity used in an experiment was estimated with a carefully regulated stop-clock and a calibrated ammeter, the latter reading to the second place of decimals. As confirmation of the readings of these two instruments, a copper coulometer was also used in some estimations.

Test experiments were performed with the ammeter, clock, and copper coulometer. The results of a typical experiment are given below :—

Weight of Copper deposited in coulometer = 0.5490 gm.  
0.5490 gm. of Cu is equivalent to  $0.5490/0.000328$   
= 1673.8 coulombs.

Ammeter reading = 1.55 amperes.

Time „ = 18 mins. 2 secs.

1.55 amp. for 18 mins. 2 secs. is equivalent to 1677 coulombs. The difference is below 0.2 per cent.

*Results of 4 experiments : using ammeter and clock.*

Weight of Substance.	Current.	Time.	Value of L.
32.9625 grms.	1.53 amps.	35 mins. 48 secs.	51.24
30.8935 grms.	1.55 amps.	32 mins. 54 secs.	50.97
30.3970 grms.	1.54 amps.	32 mins. 30 secs.	51.27
31.1485 grms.	1.54 amps.	33 mins. 5 secs.	50.72

*Experiment for check with Copper coulometer.*

33.4880 grms. Acid.

Weight of Cu deposited in coulometer = 1.0758 grms.,

Ammeter reading = 1.55,

giving a value for L, the Latent Heat of Fusion, of 50.94.

The mean value of L from the five experiments is 51.03.

The resistance of the platinum coil used in the experiments, corrected for the resistance of leads and for temperature, was 1.41 ohms.

The formula used for the calculation of L was, as before :

$$L = C^2 R t / 4.18 W \text{ gm. cal. per gram.}$$

Determinations of the value of the Molecular Depression of the Freezing-Point of this same Palmitic Acid were made with a Beckman freezing-point apparatus. The solute used was Mesitylene (B.P.  $162^\circ \text{C}$ ).

Weight of Palmitic Acid.	Weight of Mesitylene.	Depression.	E.
12.5055 grms.	0.1980 gm.	$0.57^\circ \text{C}$ .	43.24
11.3749 grms.	0.1407 gm.	$0.44^\circ \text{C}$ .	42.75
12.6547 grms.	0.1471 gm.	$0.42^\circ \text{C}$ .	43.39

E = Depression of the Freezing-Point of Palmitic Acid on the addition of 1 gm. molecular weight of mesitylene to 100 grms. of the acid.

The calculation of the value of  $L$ , from the above values of  $E$ , by means of the formula

$$E = 0.0198T^2/L,$$

gave the following results :

$$\begin{array}{ll} E = 43.24 & L = 51.6 \\ E = 42.75 & L = 52.2 \\ E = 43.39 & L = 51.44 \end{array}$$

Landolt-Börnstein, p. 1430, give  $E=44$ .

As a check on the possibility of error owing to association of the mesitylene dissolved in the acid, determinations of the lowering of the freezing-point of pure Benzene were carried out in order to see how they compared with the recognized values of  $E$  for Benzene :—

Weight of Benzene.	Weight of Mesitylene.	Depression.	$E$ .
15.3697 grms.	0.1416 grm.	0.39° C.	50.86
15.0893 grms.	0.1266 grm.	0.36° C.	51.52
16.1610 grms.	0.1941 grm.	0.518° C.	51.80

Landolt-Börnstein, p. 1427, give  $E=51.2$  for Benzene.

These determinations of the value of  $E$  show that Mesitylene is not associated in Benzene solution, and therefore it probably is not associated in solution in Palmitic Acid.

The agreement between values of  $E$  determined from these two sets of experiments removes entirely the discrepancy of nearly 20 per cent. between found and calculated values for  $E$  given in Nernst's *Lehrbuch*, 1921, p. 158, and shows that Palmitic Acid shows quite normal behaviour in this connexion.

## 2. BENZENE.

Determinations of the value of  $L$  for Benzene were also carried out in the same apparatus. The "Pure" Benzene of Kahlbaum was re-fluxed with a 25 per cent. aqueous solution of mercuric acetate, washed well with distilled water, dried with calcium chloride, re-fluxed with metallic sodium, and then fractionated. The product gave no test for thiophen with isatin, and had a boiling-point of 80.49° C. In the experiments a weighed amount of pure benzene was frozen before being put into the bath of molten benzene. It was allowed to stand in the bath until the thermometer in the centre of the solid benzene registered the same as that of the bath, 5.85° C., so that the setting-point of the Pure Benzene used was 5.85° C. Landolt-Börnstein (1912, p. 240) give B.P. 80.2°, M.P. 5.58°.

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	Weight of Benzene.	Ampere.	Time.	Value of L.
(1)	49.8705 grms.	1.53 amp.	30 mins.	29.76
(2)	55.820 grms.	1.54 amp.	33 mins.	29.63
(3)	55.247 grms.	1.53 amp.	34 mins. 2 secs.	30.45
(4)	51.3906 grms.	1.56 amp.	31 mins. 58 secs.	29.83

Average value of  $L = 29.92$  gm. cal.

Landolt-Börnstein give  $L = 30.11$ .

The resistance of the platinum coil used in these experiments was 1.479 ohms.

*Summary.*

The latent heats of fusion, and the molecular depressions of freezing-point (with mesitylene as solute), have been determined for carefully purified palmitic acid and benzene by the method described in a former communication.

	M.Pt.	S.Pt.	B.Pt.	L gm. cal. per gm.	E for 100 grm. solvent.
Palmitic acid ...	62.65° C.	62.25° C.	267- 270/100 mm.	51.03	43.13
Benzene .....	.....	5.85° C.	80.49° C.	29.92	51.39

The results remove the large discrepancy between the observed and calculated values of  $E$  in the case of palmitic acid which are given in the literature.

The authors desire to express their thanks to the Chemical Society for a grant to one of them (K. S.), which largely covered the expense of the investigation, and to Price's Candle Co. for a specially expressed sample of Palmitic Acid which they very kindly supplied.

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*CVII. Some Problems of Two-dimensional Hydrodynamics.*

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**T**HIS paper treats the motion of a cylinder in fluid when the curve of cross-section of the cylinder is a member of the series of curves given by the equations

$$x = a \cos u + \frac{1}{2}b \cos 2u \quad 0 < b < a$$

$$y = b \sin u - \frac{1}{2}b \sin 2u.$$

These curves form an interesting set and range from the well-known star-like curve with three cusps (sometimes called the three-cusped hypocycloid) when  $b$  is equal to  $a$ ,

\* Communicated by the Author.

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through the series of liqueur-bottle shapes as  $b$  decreases to  $\frac{1}{2}a$  to tadpole-like curves when  $b$  decreases through smaller values to zero. This series has been selected for treatment because it comprises curves with concave and convex arcs

Fig. 1.

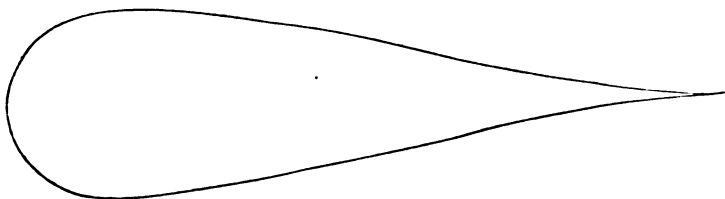


Fig. 2.

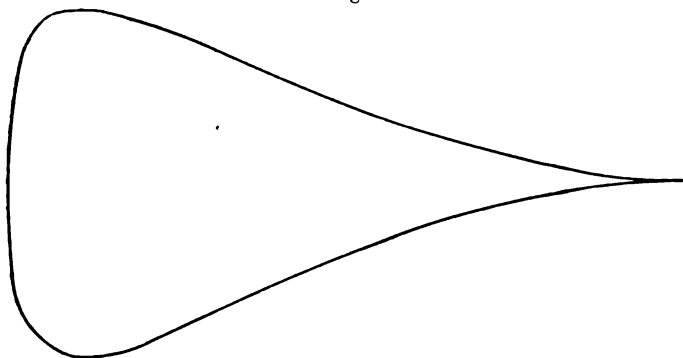
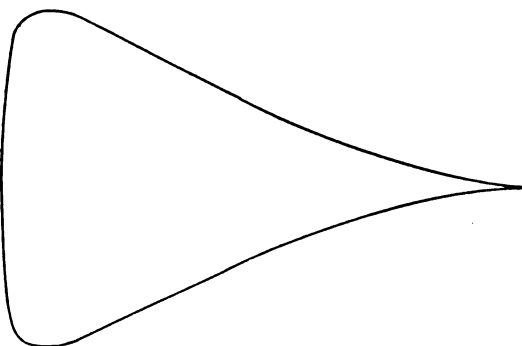


Fig. 3.



and cusps of a type not hitherto subjected to exact mathematical analysis. Further, the existence of the whole series of curves makes the results obtained of wide application; for many curves of a type resembling the liqueur-bottle type or the tadpole type can be treated at least approximately by interpolation between the curves of this series.

In this paper we work out a number of problems of classical hydrodynamics associated with a cylinder whose cross-section is of the specified type. Thus, we discuss first the motion of a fluid streaming past such a cylinder with a uniform velocity. Next we discuss the motion when the cylinder moves with uniform translational velocity in a fluid at rest at a great distance. Next we take the motion when the cylinder rotates with uniform angular velocity about its axis in a fluid at rest at a great distance. Next we discuss the motion when there is circulation of the fluid round the cylinder.

Fig. 4.

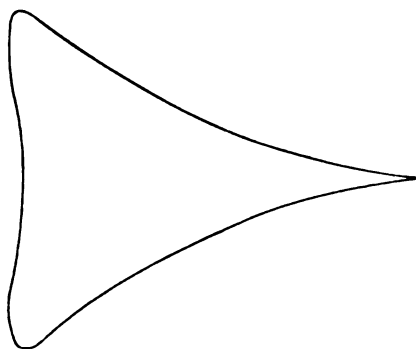
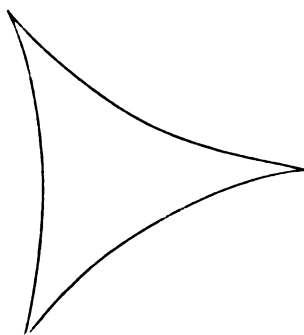


Fig. 5.



The development of aerodynamical research into the usefulness of wing profiles of various types in aerofoils of high aspect ratio, lends special interest to new results of the type we are here concerned with, especially in the case when the curve of cross-section has a cusp which constitutes the trailing edge of the wing. But it is well known that when the velocity in the neighbourhood of the wing becomes large at any point



classical hydrodynamics becomes quite inapplicable, and a new treatment which takes into account the viscosity of the air becomes imperative. Now, in accordance with the well-recognized theory of hydrodynamics, there is, in general, an infinite velocity at the cusp associated with each of the types of motion we have mentioned. But, it is not so well recognized that there exist in general combinations of any two of these three distinct types of motion which give a uniformly finite velocity at all points. The fact that it is possible to get a uniformly finite velocity in the case of a combination of translation and circulation has been noticed by Joukowsky\*, and has led to the formation of his assumption now current in the Circulatory Theory of Lift in Aerodynamics†. For these reasons it has been deemed worth while to work out various combinations of the pure types, which have the characteristic that the velocity is everywhere finite, in addition to the pure types themselves. These mixed motions are evidently applicable to aerofoils of high aspect ratio when the various constants involved are so chosen that the velocity, now always finite, is sufficiently small.

### 1. Description of the Curves.

The equation of the curves of cross-section is taken in the form

$$\begin{aligned}x &= x(u) = a \cos u + \frac{1}{2}b \cos 2u \\y &= y(u) = b \sin u - \frac{1}{2}b \sin 2u,\end{aligned}\quad 0 \leq b \leq a$$

in terms of the parameter  $u$  which increases uniformly from  $-\pi$  to  $+\pi$  on a complete description of the curves. The curves have one axis of symmetry, namely, the  $x$ -axis; but they are not symmetrical about the  $y$ -axis under any circumstances. We have

$$\begin{aligned}dx/du &= -a \sin u - b \sin 2u, \\dy/du &= b \cos u - b \cos 2u,\end{aligned}$$

and in consequence, if  $\psi$  is the angle made with the axis of  $x$  by the tangent to the curve at any point  $u$ ,

$$\tan \psi = b (\cos u - \cos 2u) / \sin u (a + 2b \cos u).$$

\* See N. Joukowsky, *Aérodynamique* (traduit du russe par S. Drzewiecki), Gauthier-Villars, Paris, 1916, chapter vi.

† See A. R. Low, "Circulation Theory of Lift," Report of the International Air Congress, London, 1923; also, "Hydrodynamics in its Application to Aeronautics," 'Dictionary of Applied Physics,' vol. v. p. 187 (1923).

Thus at the point  $u=0$ ,  $\psi$  is  $\pi$ ; and at the point  $u=\pi$ ,  $\psi=3\pi/2$ . Whatever the value of the proper fraction  $b/a$ , there is a cusp at the point  $u=0$ , and there is a rounded base in the neighbourhood of the point  $u=\pi$ . Further, apart from the point  $u=0$ , a curve belonging to the series has its tangent parallel to the axis of  $x$  only at the points given by  $\cos u = -\frac{1}{2}$ , i. e. at the points  $u = \pm 2\pi/3$ . At these points  $y = \pm 3\sqrt{3}b/4$  and  $x = -\frac{1}{2}(a + \frac{1}{2}b)$ . The maximum width of the curve is, in consequence,  $3\sqrt{3}b/2$ , and the curve attains this width at points at a distance  $-\frac{1}{2}(a + \frac{1}{2}b)$  from the origin of coordinates, measured along its axis of symmetry, the  $x$ -axis. The curve cuts its axis of symmetry at  $x = a + \frac{1}{2}b$  and at  $x = -a + \frac{1}{2}b$ ; thus its major axis is of length  $2a$ . Apart from the points  $u = \pm 2\pi/3$ , the tangent to the curve is parallel to the  $y$ -axis only when

$$a + 2b \cos u = 0.$$

Thus, it is only when  $\frac{1}{2}a < b < a$  that there are any such points. As  $b$  ranges from  $\frac{1}{2}a$  to  $a$ , these points range from  $u=\pi$  when  $b=\frac{1}{2}a$  to  $u=\pm 2\pi/3$  when  $b=a$ . Further,

$$d^2x/du^2 = -(a \cos u + 2b \cos 2u),$$

$$d^2y/du^2 = -b(\sin u - 2 \sin 2u).$$

Thus,

$$\begin{aligned} f(u) &= dx/du \cdot d^2y/du^2 - dy/du \cdot d^2x/du^2 \\ &= l(a \cos u + 2b \cos 2u)(\cos u - \cos 2u) \\ &\quad + b(a \sin u + b \sin 2u)(\sin u - 2 \sin 2u) \\ &= b(a - 2b + (2b - a) \cos 2u \cos u + (b - 2a) \sin 2u \sin u) \\ &= b(a - 2b + (b - \frac{1}{2}a)(\cos u + \cos 3u) \\ &\quad + (\frac{1}{2}b - a)(\cos u - \cos 3u)) \\ &= b(\frac{3}{2}(a - b)(1 - \cos u) - \frac{1}{2}(a + b)(1 - \cos 3u)) \\ &= b(a + b)(k^2 \sin^2 u/2 - \sin^2 3u/2), \end{aligned}$$

where

$$k = (3(a - b)/(a + b))^{\frac{1}{2}}.$$

Now, the curve is concave to the axis of  $x$  when  $f(u)$  is positive, and convex when  $f(u)$  is negative, and when  $f(u)$  vanishes there is a point of zero curvature. Now,  $f(u) \geq 0$  according as

$$|\sin 3u/2| \geq k |\sin u/2|.$$

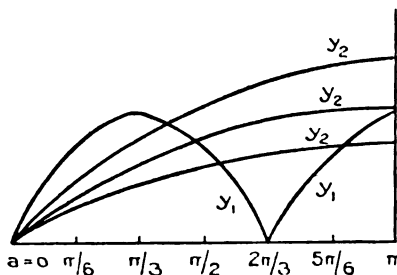
We give a diagram showing

$$y_1 = \sin 3u/2$$

and

$$y_2 = k \sin u/2,$$

Fig. 6.



$y_2$  being shown for various values of  $k$ , ranging from zero when  $a$  and  $b$  are equal through the value unity when  $b = \frac{1}{2}a$ , to the value  $\sqrt{3}$  when  $b$  is zero. We need discuss only the cases when  $u$  is positive, since the curve is symmetric about the axis of  $x$ . It will be seen that whatever the value of  $k$ ,  $f(u)$  is negative from  $u=0$  to a certain point  $u=u_0$ , which is less than  $2\pi/3$ , and is less remote from  $2\pi/3$  as  $k$  increases. When  $k$  is less than unity, *i. e.* when  $b$  is less than  $2a$ ,  $f(u)$  is positive from  $u_0$  to  $\pi$ . With the curves for which  $b$  is less than  $\frac{1}{2}a$ , we therefore have a convex arc from  $u=0$  to  $u=u_0$  and then a concave arc from  $u=u_0$  to  $u=\pi$ :  $u=u_0$  is, of course, a point of inflexion. If, however,  $b$  is greater than  $\frac{1}{2}a$ , in general there is still a convex arc from  $u=0$  to  $u=u_0 < 2\pi/3$ , a point of inflexion at  $u_0$  and then a concave arc; but in these cases the concave arc is terminated at a point  $u_1$  lying between  $2\pi/3$  and  $\pi$ , which is a point of inflexion, and the curve is then again convex to the point  $u=\pi$ . This alternation of convexity and concavity in the series of curves for which  $b$  is greater than  $\frac{1}{2}a$  has interesting effects on the various solutions of hydrodynamical problems associated with cylinders with these curves as cross-sections with which we shall presently deal.

To find the values of  $u_0$  and  $u_1$ , we put

$$\begin{aligned} f(u) &= b(a+b)(k^2 \sin^2 u/2 - \sin^2 3u/2) \\ &= b(a+b)(\sin^2 u/2(k^2 - (4 \cos^2 u/2 - 1)^2)) \\ &= b(a+b) \sin^2 u/2 (k^2 - (2 \cos u + 1)^2). \end{aligned}$$

Thus,  $f(u)$  vanishes when  $u=0, \pi$ , and when

$$\cos u = -\frac{1}{2} \pm \frac{1}{2}k.$$

In consequence,

$$\cos u_0 = -\frac{1}{2}(1-k),$$

$$\cos u_1 = -\frac{1}{2}(1+k);$$

$u_0$  is evidently always real, since  $k$  ranges from zero to  $\sqrt{3}$  only;  $u_1$ , on the other hand, only exists when  $k$  lies between zero and unity. We have, indeed, when  $k=0$  and  $a$  and  $b$  are equal

$$u_0 = u_1 = 2\pi/3,$$

and when  $k=1$  and  $b=\frac{1}{2}a$

$$u_0 = \pi/2, \quad u_1 = \pi,$$

and when  $k=\sqrt{3}$  and  $b$  is zero

$$u_0 = 68\frac{1}{2}^\circ.$$

It will be noticed that in the extreme case when  $a=b$ ,  $u_0=u_1$  and a cusp takes the place of the points of inflexion.

Diagrams of various members of the series of curves are given in figs. 1-5. The following values of the proper fraction  $b/a$  have been selected for illustration:—

$$2/10, \quad 2/5, \quad 2/4, \quad 2/3, \quad 2/2.$$

The extreme case when  $a$  and  $b$  are equal is the well-known hypocycloid with three cusps; the extreme case when  $b$  vanishes is the terminated straight line.

### *Streaming past a Cylinder.*

Consider the W-function

$$W_0 = \phi_0 + i\psi_0$$

given by

$$W_0 = -q_0 z e^{-i\gamma},$$

so that

$$\phi_0 = -q_0(x \cos \gamma + y \sin \gamma),$$

$$\psi_0 = -q_0(y \cos \gamma - x \sin \gamma),$$

where  $\phi_0$  is the velocity potential and  $\psi_0$  the stream function associated with some motion. Since

$$-\partial\phi_0/\partial x = q_0 \cos \gamma,$$

$$-\partial\phi_0/\partial y = q_0 \sin \gamma,$$

it evidently represents motion of fluid streaming with velocity  $q_0$  in a direction making an angle  $\gamma$  with the axis of  $x$ .

Now suppose that a cylinder whose cross-section is the curve  $c$  whose equation is

$$x = a \cos u + \frac{1}{2}b \cos 2u \quad 0 \leq b \leq a$$

$$y = b \sin u - \frac{1}{2}b \sin 2u$$

is placed in the stream of fluid and held at rest. The presence of the cylinder will disturb the motion represented by  $W_0$ , described above. Suppose

$$W_1 = \phi_1 + i\psi_1$$

represents the disturbing effect of the cylinder, so that the motion in the presence of the cylinder is given by

$$W = W_0 + W_1.$$

Then  $\psi_1$  must be a solution of Laplace's equation evanescent on the circle at infinity, without singularities between the curve  $c$  and the circle at infinity, and, finally, on the curve  $c$   $\psi_0 + \psi_1$  must be constant.

Now, on the curve  $c$ ,

$$\begin{aligned} z &= x + iy \\ &= a \cos u + ib \sin u + \frac{1}{2}b e^{-2iu}. \end{aligned}$$

Then taking the transformation

$$z = a \cos w + ib \sin w + \frac{1}{2}b e^{-2i\pi},$$

where  $w = u + i\pi$ , we ensure that on the curve  $c$ ,  $v = 0$ . Further,

$$z = \frac{1}{2}(a+b)e^{i\pi} + \frac{1}{2}(a-b)e^{-i\pi} + \frac{1}{2}b e^{-2i\pi},$$

and consequently, on the circle at infinity,  $v = -\infty$ .

Now, in terms of  $u$ , on the curve  $c$ ,

$$\psi_0 = -q_0\{b \sin u \cos \gamma - a \cos u \sin \gamma - \frac{1}{2}b \sin (2u + \gamma)\}.$$

If now we write

$\psi_1 = -q_0\{b \cos \gamma e^{\pi} \sin u - a \sin \gamma e^{\pi} \cos u - \frac{1}{2}b e^{2\pi} \sin (2u + \gamma)\}$ ,  $\psi_1$  is certainly a solution of Laplace's equation, which is evanescent on the circle at infinity and without singularities between  $c$  and the circle at infinity, and, in addition, on the curve  $c$

$$\psi_1 = (\psi_1)_{v=0} = q\{b \cos \gamma \sin u - a \sin \gamma \cos u - \frac{1}{2}b \sin (2u + \gamma)\}.$$

Thus,  $\psi_0 + \psi_1$  is zero on the curve  $c$ . We therefore have  $\psi_1$  as above, and in consequence

$$W_1 = -q_0\{b \cos \gamma e^{-i\pi} + ia \sin \gamma e^{-i\pi} - \frac{1}{2}b e^{-2i\pi - i\gamma}\}$$

and

$$\phi_1 = -q_0\{b \cos \gamma e^{\pi} \cos u + a \sin \gamma e^{\pi} \sin u - \frac{1}{2}b e^{2\pi} \cos (2u + \gamma)\}$$

Also

$$\begin{aligned} W &= -q_0 z e^{-i\gamma} \\ &= -q_0 e^{-i\gamma} \left\{ a \cos w + ib \sin w + \frac{1}{2} e^{-2iw} \right\}. \end{aligned}$$

Therefore

$$\begin{aligned} W &= W_0 + W_1 \\ &= -q_0(a+b) \cos(w-\gamma), \end{aligned}$$

giving

$$\begin{aligned} \phi &= -q_0(a+b) \cos(u-\gamma) \cosh v, \\ \psi &= q_0(a+b) \sin(u-\gamma) \sinh v. \end{aligned}$$

The velocity  $q$  at any point  $u$  on the curve is given by

$$q = -q_0(a+b) \sin(u-\gamma) / |dz/dw|_{v=0}$$

in the direction  $u$  increasing, *i. e.* along the arc of the curve.

Now,

$$dz/dw = i\left\{ \frac{1}{2}(a+b)e^{i\pi} - \frac{1}{2}(a-b)e^{-i\pi} - be^{-2i\pi} \right\}.$$

Thus on the curve  $c$

$$\begin{aligned} |dz/dw|^2 &= |dz/dw|^2_{v=0} = (a \sin u + b \sin 2u)^2 \\ &\quad + (b \cos u - b \cos 2u)^2. \end{aligned}$$

Evidently at  $u=0$ ,  $|dz/dw|$  vanishes and the velocity is infinite except in the particular case when  $\gamma=0$ , that is, when the direction of streaming in the undisturbed field is parallel to the tangent to the curve at the cusp.

## 2. Translational Motion.

We may also investigate the motion represented by this  $W$ -function,

$$W_1 = q_0 \{ b \cos \gamma e^{-i\pi} + ia \sin \gamma e^{-i\pi} - \frac{1}{2} b e^{-2i\pi} \},$$

alone. It is obtained by superposing on  $W$ , the  $W$ -function  $W_0$ . Thus, it represents the motion when the cylinder is moving in a fluid at rest at infinity with a velocity  $q_0$  in a direction opposite to the direction of the streaming in the undisturbed field discussed in the foregoing case, *i. e.* in the direction making an angle  $\pi+\gamma$  with the axis of  $x$ . The stream function and velocity potential for this motion are given by

$$\begin{aligned} \psi_1 &= q_0 \{ b \cos \gamma e^v \sin u - a \sin \gamma e^v \cos u - \frac{1}{2} b e^{2v} \sin(2u+\gamma) \}, \\ \phi_1 &= -q_0 \{ b \cos \gamma e^v \cos u + a \sin \gamma e^v \sin u - \frac{1}{2} b e^{2v} \cos(2u+\gamma) \}. \end{aligned}$$

The velocity at any point  $u$  is  $q$  given by

$$q^2 = \{ (\partial \phi_1 / \partial u)^2 + (\partial \phi_1 / \partial v)^2 \} / |dz/dw|_{v=0},$$

and again, the velocity at the cusp is in general infinite.

The kinetic energy of the fluid per unit length  $T$  is given by

$$\begin{aligned} T &= -\frac{1}{2}\rho \int_c \phi d\psi \\ &= \frac{1}{2}\rho q^2 \int_0^{2\pi} (b \cos \gamma \cos u + a \sin \gamma \sin u - \frac{1}{2}b \cos (2u + \gamma)) \\ &\quad \times (b \cos \gamma \sin u + a \sin \gamma \cos u - b \cos (2u + \gamma)) du \\ &= \frac{1}{2}\rho q^2 \pi (b^2 \cos^2 \gamma + a^2 \sin^2 \gamma + \frac{1}{2}b^2). \end{aligned}$$

The area of the cross-section of the curve  $c$  is  $A$ , given by

$$\begin{aligned} A &= \frac{1}{2} \int_0^{2\pi} (x dy/du - y dx/du) du \\ &= \frac{1}{2}b \int_0^{2\pi} \{ (a \cos u + \frac{1}{2}b \cos 2u)(\cos u - \cos 2u) \\ &\quad + (\sin u - \frac{1}{2} \sin 2u)(a \sin u + \beta \sin 2u) \} du \\ &= \pi b(a - \frac{1}{2}b). \end{aligned}$$

Thus

$$T = \frac{1}{2}\rho q^2 A \{ \mu_x \cos^2 \gamma + \mu_y \sin^2 \gamma \},$$

with

$$\begin{aligned} \mu_x &= \frac{3}{2}b/(a - \frac{1}{2}b), \\ \mu_y &= (a^2 + \frac{1}{2}b^2)/b(a - \frac{1}{2}b). \end{aligned}$$

The constants  $\mu_x$  and  $\mu_y$  may be called the coefficients of translational mass in the  $x$ -direction and in the  $y$ -direction associated with the cylinder whose cross-section is the curve  $c$ . We give a table of the coefficients  $\mu_x$  and  $\mu_y$  for various values of the proper fraction  $b/a$ .

$b/a$ .	$\mu_x$ .	$\mu_y$ .
0	0.000	$\infty$
1	1.579	10.5789
2	3.333	5.6667
3	5.294	4.0980
4	7.500	3.3750
5	1.0000	3.0000
6	1.2857	2.8243
7	1.6154	2.7346
8	2.0000	2.7500
9	2.4545	2.8384
10	3.0000	3.0000

It will be remarked in this table that for the cusped hypocycloid given by  $b/a=1$  the values of  $\mu_x$  and  $\mu_y$  are the same.

This result involves the consequence that in every direction whatever the coefficient of hydrodynamical mass due to translational motion is the same. This result is a particular case of the general theorem that if  $c$  the curve of the cross-section repeats itself  $n$  times on a complete description, where  $n$  is greater than two, the coefficient of hydrodynamical mass due to translational motion in any direction is the same. For suppose that  $\mu_x$  and  $\mu_y$  are the coefficients associated with two perpendicular directions. Then the coefficient associated with a direction making an angle  $2\pi/n$  with the first is given by

$$\mu_x \cos^2 2\pi/n + \mu_y \sin^2 2\pi/n.$$

But this must be identically equal to  $\mu_x$  itself, owing to the symmetry of the curve. Therefore

$$\mu_x \cos^2 2\pi/n + \mu_y \sin^2 2\pi/n = \mu_x,$$

and the conclusion that  $\mu_x$  and  $\mu_y$  are equal follows. Now the hypocycloid with three cusps which we deal with when  $a$  and  $b$  are equal repeats itself three times, and it consequently follows that the two coefficients associated with the direction  $z$  and  $y$  and the coefficients associated with any other direction whatever are equal.

It will further be noticed that  $\mu_y$  as a function of the proper fraction  $b/a$ , which it will be convenient to call  $\lambda$ , has a minimum near the value  $\lambda = .7$ . We have, in fact,

$$\begin{aligned} \mu_y &= (2a^2 + b^2)/b(2a - b) \\ &= (2 + \lambda^2)/\lambda(2 - \lambda). \end{aligned}$$

Then  $d\mu_y/d\lambda = 0$ ,

when  $2(2 - \lambda) = 2(2 + \lambda^2)(1 - \lambda)/(2\lambda - \lambda^2)^2$ ,

i.e. when  $\lambda = 1$  or

$$\lambda^2 + 2\lambda - 2 = 0,$$

i.e. when  $\lambda = \pm \sqrt{3} - 1$ .

The significance value of  $\lambda$  is evidently  $\sqrt{3} - 1 = .7321$ .

### 3. Rotating Cylinders.

Suppose that this cylinder whose cross-section is the curve  $c$  is rotating with uniform angular velocity  $\omega$  about its axis. The stream function  $\psi$  associated with the motion must be a solution of Laplace's equation, as before, and evanescent at infinity and without singularities between  $c$



and the circle at infinity. Further we must have

$$\psi + \frac{1}{2}\omega r^2$$

constant on the curve  $c$ . Now in terms of  $u$ , on the curve  $c$ ,

$$\begin{aligned} r^2 &= (a \cos u + \frac{1}{2}b \cos 2u)^2 + (b \sin u - \frac{1}{2}b \sin 2u)^2 \\ &= a^2 \cos^2 u + b^2 \sin^2 u + \frac{1}{4}b^2 + ab \cos u \cos 2u - b^2 \sin u \sin 2u \\ &= \frac{1}{2}a^2 + \frac{3}{4}b^2 + \frac{1}{2}(ab - b^2) \cos u + \frac{1}{2}(ab + b^2) \cos 3u \\ &\quad + \frac{1}{2}(a^2 - b^2) \cos 2u. \end{aligned}$$

Thus writing

$$\begin{aligned} \psi &= -\omega \left\{ \frac{1}{4}b(a-b)e^v \cos u + \frac{1}{4}(a^2 - b^2)e^{2v} \cos 2u \right. \\ &\quad \left. + \frac{1}{4}b(a+b)e^{3v} \cos 3u \right\} \end{aligned}$$

we obtain a value for  $\psi$  which satisfies all the conditions. We therefore have also

$$\begin{aligned} \phi &= -\omega \left\{ \frac{1}{4}b(a-b)e^v \sin u + \frac{1}{4}(a^2 - b^2)e^{2v} \sin 2u \right. \\ &\quad \left. + \frac{1}{4}b(a+b)e^{3v} \sin 3u \right\}. \end{aligned}$$

At any point  $u$  on the curve the velocity  $q$  is given by

$$\begin{aligned} q &= -\omega \left\{ \frac{1}{4}b(a-b) \cos u + \frac{1}{2}(a^2 - b^2) \cos 2u \right. \\ &\quad \left. + \frac{3}{4}b(a+b) \cos 3u \right\} / \left| \frac{dz}{dw} \right|_{v=0}. \end{aligned}$$

The velocity is evidently infinite at the cusp  $u=0$ , for at that point  $q$  is given by

$$q = (q)_{u=0} = -\omega(ab + \frac{1}{2}u^2) / \left| \frac{dz}{dw} \right|_{u=v=0}.$$

It will be remarked that this infinity in  $q$  at the cusp, since it arises from the zero of  $\left| \frac{dz}{dw} \right|_{v=0}$  at that point, is of the same type as the infinity for  $q$  in the case of translational motion.

The kinetic energy of the liquid due to the rotation of the liquid T say per unit length is given by

$$\begin{aligned} T &= -\frac{1}{2}\rho \int \phi d\psi \\ &= \frac{1}{32}\rho\omega^2 \int_0^{2\pi} (b(a-b) \sin u + (a^2 - b^2) \sin 2u + b(a+b) \sin 3u) \\ &\quad \times (b(a-b) \sin u + 2(a^2 - b^2) \sin 2u + 3b(a+b) \sin 3u) du \\ &= \frac{1}{32}\pi\rho\omega^2 \{ b^2(a-b)^2 + 2(a^2 - b^2)^2 + 3b^2(a+b)^2 \} \\ &= \frac{1}{16}\pi\rho\omega^2 \{ a^4 + 2ab^3 + 3b^4 \}. \end{aligned}$$

We may introduce  $\nu$  by the equation

$$T = \frac{1}{2}\nu\rho A k^2 \omega^2$$

where  $k$  is the radius of gyration of unit length of the

cylinder about its axis and call  $\nu$  the coefficient of hydrodynamical mass associated with rotation. Then

$$Ak^2\nu = \frac{\pi}{8}(a^4 + 2ab^3 + 3b^4).$$

It is convenient to record here the value of  $k$  for the particular series of cross-sections dealt with in this paper. We have, if  $k_x$  and  $k_y$  are the radii of gyration about the axis of  $x$  and  $y$

$$\begin{aligned} Ak_x^2 &= \int_0^{2\pi} y^2 x dx \\ &= b^3 \int_0^{2\pi} [\sin^2 u + \frac{1}{4} \sin^2 2u - \sin u \sin 2u] [a \cos u \\ &\quad + \frac{1}{2} b \cos 2u] [\cos u - \cos 2u] du \\ &= b^3 \int_0^{2\pi} [\frac{5}{8} - \frac{1}{2} \cos 2u - \frac{1}{8} \cos 4u - \frac{1}{2} (\cos u - \cos 3u)] \\ &\quad \times [\frac{1}{2}(a - \frac{1}{2}b) + \frac{1}{2}a \cos 2u - \frac{1}{4}b \cos 4u \\ &\quad + \frac{1}{2}(\frac{1}{2}b - a)(\cos u + \cos 3u)] du \\ &= b^3 \pi [\frac{5}{2}(a - \frac{1}{2}b) - \frac{1}{4}a + \frac{1}{3}\frac{1}{2}b] \\ &= b^3 \pi [\frac{3}{8}a - \frac{9}{32}b] \\ &= 3b^3 \frac{\pi}{32} (4a - 3b). \end{aligned}$$

Next, in the same manner we may prove that

$$Ak_y^2 = \frac{1}{32} b \pi (8(a^3 - a^2b) + 4ab^2 - b^3).$$

Thus

$$\begin{aligned} Ak^2 &= Ak_x^2 + Ak_y^2 \\ &= \frac{\pi b}{16} (4(a^3 - a^2b) + 8ab^2 - 5b^3). \end{aligned}$$

We therefore have the result

$$r = 2(a^4 + 2ab^3 + 3b^4)/b(4a^3 - 4a^2b + 8ab^2 - 5b^3),$$

or in terms of the proper fraction  $\lambda = b/a$ ,

$$r = 2(1 + 2\lambda^3 + 3\lambda^4)/\lambda(4 - 4\lambda + 8\lambda^2 - 5\lambda^3).$$

#### 4. Circulation about a Cylinder.

Suppose that there is circulation  $k$  round the cylinder of cross-section  $c$ . Then the motion may be represented by the function

$$W = \phi + i\psi = + \frac{k}{2\pi} (u + iv) = + \frac{k}{2\pi} w,$$

where, as before,

$$z = a \cos w + ib \sin w + \frac{1}{2} b e^{-2iw}.$$

For, if  $\phi$  be the velocity potential, the circulation is given by

$$\int_c -\partial\phi/\partial s ds$$

and this is equal to

$$-\int_0^{2\pi} \frac{k}{2\pi} ds,$$

which is evidently equal to  $-k$ . The velocity  $q$  at any point on the cylinder is given by

$$q = -k/2\pi \mid dz/dw \mid_{v=0}$$

in the direction of the arc of the curve, measured with  $u$  increasing. Again we have an infinity for the velocity  $q$  at the cusp  $u=0$ , and again this infinity is of precisely the same type as in the problems of translational and rotational motion.

### 5. Mixed Motions.

It has been pointed out that when a cylinder rotates about its axis or when there is circulation about the cylinder, the existence of the cusp on the curve  $c$  of its cross-section involves an infinite velocity at that point. This has also been shown to be the case when there is translational motion past the cylinder, except in the particular case when the direction of the streaming at a great distance is parallel to the tangent to the curve  $c$  at the cusp.

Now, in all these cases where the velocity is infinite at the cusp, it is infinite like

$$1/\mid dz/dw \mid_{v=u=0}.$$

Linear combinations of these three pure types of motion therefore evidently exist in which the velocity at the cusp is no longer infinite as it is, in general, in motions of the pure types when they occur separately. Thus suppose we consider a *mixed* motion in which circulation about the cylinder is superposed on streaming past. We may superpose the motion of (2) on the motion of (4), and we then get

$$W = -q_0(a+b) \cos(w-\gamma) + kw/2\pi,$$

giving

$$\phi = -q_0(a+b) \cos(u-\gamma) \cosh r + \kappa u/2\pi.$$

Then on the curve  $c$

$$-\partial\phi/\partial u = -(q_0(a+b) \sin(u-\gamma) + \kappa/2\pi), \quad \partial\phi/\partial r = 0,$$

and

$$\mid dz/dw \mid^2 = (a \sin u + b \sin 2u)^2 + b^2 (\cos u - \cos 2u)^2.$$

Thus  $q$  on the curve is given by

$$q = -(q_0(a+b) \sin(u-\gamma) + k/2\pi) / |dz/dw|_{\tau=0},$$

and, in general,  $q$  is infinite at the cusp  $u=0$ .

If the ratio of  $k$  to  $q_0$  is so chosen that

$$k = +2\pi q_0(a+b) \sin \gamma$$

the velocity at the cusp is not infinite. We have, in fact,

$$q = q_0(a+b) (\sin(u-\gamma) + \sin \gamma) / |dz/dw|_{\tau=0},$$

so that at the cusp

$$q^2 = (q^2)_{u=0} = [q_0(a+b) \cos \gamma / (a+2b)]^2.$$

With this combination of translational motion and circulation an interesting type of motion results in which the velocity is never infinite on the curve  $c$  and, indeed, never infinite outside the curve. And it is to be remarked that this characteristic of the motion can be retained, whatever the direction of the translational velocity, by suitably choosing the ratio of  $k$  to  $q_0$ .

It is well known \* that streaming past a cylinder together with circulation about the cylinder gives rise to a resultant force on the cylinder which is equal to  $\rho k q_0$  per unit length, where  $\rho$  is the density of the surrounding fluid. And this force acts in a direction  $\pi/2$  from the direction of streaming at a great distance measured in the direction opposite to that of the positive circulation. This force may be called the Lift on the cylinder. It is interesting to notice the fact that classical hydrodynamics gives a resultant force on the cylinder in this mixed motion which further has the important characteristic that the velocity of the cylinder is always finite. An important part of the requirements of the aerodynamics relating to the wings of aeroplanes is therefore satisfied before the viscosity of the air is taken into account at all; for on the one hand there is a resultant force on the cylinder, although in the case of all pure motions there is none, and on the other hand the velocity being never infinite may under suitable circumstances be kept within reasonable limits and the pressure  $p$  given by

$$p_0 - p = \frac{1}{2} \rho (q^2 - q_0^2)$$

(where  $p_0$  is the pressure at a great distance) will never be

\* See Lamb, 'Hydrodynamics' (5th edition), pp. 76, 647; also Joukowski, *loc. cit.* chapter vi. § 18.

negative, and we are therefore dealing with a motion which in this respect at least is physically possible in an inviscid fluid. This fact is the analytical basis of the famous Joukowski assumption in the Circulation Theory of Lift now under discussion in Aerodynamics\*.

It is also evident that translational and rotational motion can be combined so as to give an everywhere finite velocity. For superposing the rotational motion of (3) on the translational velocity of (2) we have

$$\begin{aligned}\phi = -q_0\{ & (b \cos \gamma \cos u + a \sin \gamma \sin u)e^r - \frac{1}{2}be^{2r} \cos(2u + \gamma) \frac{1}{2} \\ & - \omega\{\frac{1}{4}b(a-b)e^r \sin u + \frac{1}{4}(a^2-b^2)e^2 \sin 2u \\ & + \frac{1}{4}b(a+b)e^{3r} \sin 3u\}\end{aligned}$$

Evidently if we choose the ratio of  $\omega$  to  $q_0$ , so that

$$\omega(\frac{1}{2}a^2 + ab) = -q_0(a+b) \sin \gamma,$$

$q$ , the velocity, will not be infinite at the cusp. Thus with the particular combination of translational motion  $q_0$  in any direction  $\gamma$  with the appropriate rotational motion with angular velocity  $\omega$  given by

$$\omega = -\frac{2(a+b)}{a(a+2b)}q_0 \sin \gamma,$$

the velocity  $q$  is always finite and another type of motion is therefore available in which an infinite velocity is not associated with the cusp on the cross-section of the cylinder.

It is also evidently possible to combine circulation and rotation in the same way, so as to obtain a motion in which the velocity is everywhere finite—and this in spite of the cusp on the curve of cross-section of the cylinder.

\* The assumption of Joukowski should be studied in connexion with the pioneer work of Lanchester. See F. W. Lanchester, 'Aerodynamics,' London, 1911, § 189.

Excellent material obtained from actual experiments with full sized aerofoils and with model aerofoils suitable for the testing of the Lanchester-Joukowski theory of Lift is to be found in 'Aeroplane Design,' by Andrews and Benson, London, 1920, chapter iii. 'The Properties of Aerofoils and Aerodynamic Bodies,' by Judge, London, 1917, chapter ii., and in other text-books.

CVIII. *The Diffusion of Mercury and of Iodine Vapours through Nitrogen.* By J. M. MULLALY and H. JACQUES\*.

**D**IFFUSION of the vapours arising from liquids or solids and passing through various gases is well known to give statistical measures of the mechanical interactions of the molecules concerned. Few elementary vapours have been investigated in this respect, because it has been difficult to experiment with substances slightly volatile. Following the speculations of Stefan (*Wien. Ber.* lxxv. p. 323, 1872), the vapours of water and of many carbon compounds were early investigated by Winkelmann (*Ann. d. Physik*, xxii. p. 1, 1884 and vols. following). Lately Le Blanc and Wuppermann (*Zeit. f. Phys. Chem.* xci. p. 143, 1916) have determined the rates of evaporation of similar liquids in air under more refined conditions.

The present investigation, mentioned already in a summary account (Mullaly, 'Nature,' cxiii. p. 711, 1924), is undertaken primarily as a test of an experimental method, prior to the application of this method to further problems of diffusion.

#### THE METHOD.

For establishing the gradients of vapour concentration necessary for diffusion in a steady state along a uniform tube, advantage has been taken of chemical combination between two diffusing vapours, and the consequent precipitation of both as solid products.

The two vapours, of mercury and of iodine, are allowed to diffuse from the free elements situated at the opposite ends of a closed glass tube containing nitrogen. As fast as the vapours diffuse towards one another, they combine and deposit the iodides of mercury in a region of the tube where they meet.

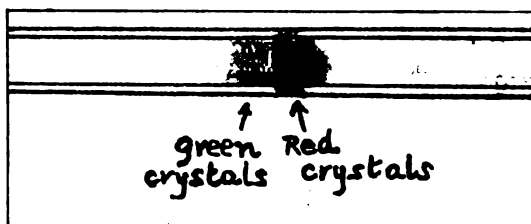
The deposit appears first as a narrow ring across the axis of the tube. On increasing in bulk, the ring spreads into a band of width comparable with the diameter of the tube, and can then be seen to contain both mercuric and mercurous iodides, the former in red crystals on the side where iodine exceeds in concentration, the latter in yellow-green crystals on that where mercury predominates. Fig. 1 is a diagram of a typical deposit. As there depicted, crystals of the two colours are separated by a very definite boundary.

\* Communicated by Prof. F. A. Lindemann, F.R.S.

For a knowledge of the gradients, it is necessary to measure the distance of the deposit from the ends of the tube, that is from the points of vaporization, and, in addition, to know the concentrations (or partial pressures) of each diffusing vapour at the points of vaporization and deposition.

The concentration of mercury vapour over the meniscus has been taken from the vapour-pressure measurements of Knudsen (1909) and of Haber (1914), together with those of Egerton (*Phil. Mag.* xxxiii. p. 33, 1917, and later communications). There seems now to be little uncertainty as to the vapour-pressure of mercury.

Fig. 1.



Over the iodide deposit in the region where combination occurs, the concentration of mercury vapour is taken to be zero. From the determinations of the vapour-pressure of mercuric iodide by Wiedemann, Stelzner, and Nideschulte (*Ber. Deut. phys. Ges.* iii. p. 161, 1905), it is evident that the concentration of mercury is negligibly small over portions of the deposit consisting of this salt. The concentration of mercury may be slightly greater over portions of the deposit which contain mercurous iodide, and there are few data to which reference could be made. That the concentration cannot be much greater is shown by the fact that the mercurous iodide is plentifully deposited beside the mercuric salt.

The concentration of iodine vapour over the iodine crystals has been computed as a mean from the direct measurements of Baxter, Hickey, and Holmes (*Journ. Amer. Chem. Soc.* 1907), and those of Naumann (*Diss.*, Berlin, 1907), determined in the laboratory of Nernst.

The maximum concentration of iodine at the deposit has been ignored.

Mercury is effectively absent from the region traversed by diffusing iodine, the dissociation constant of mercuric iodide being extremely small. Similarly the region traversed

by mercury vapour is sensibly free from iodine. Each vapour thus diffuses through nearly pure nitrogen.

According to equation

$$D_{12} \frac{\partial c_1}{\partial l} = \frac{1}{A} \frac{\Delta m_1}{\Delta t}, \quad \dots \dots (1)$$

which represents diffusion through one another of two gases crossing a given cross-section A of a long uniform tube, it is requisite for the determination of the coefficient  $D_{12}$  to know both the mass  $\Delta m_1$  of either gas which traverses the area in a short period  $\Delta t$ , and the gradient of concentration

of the same gas  $\frac{\partial c_1}{\partial l}$  across this area. The coefficient  $D_{12}$

and the gradient  $\frac{\partial c_1}{\partial l}$  are constant along the axis, so long as

the concentration of the gas denoted by suffix I (the vapour) is everywhere small compared with that of the other (nitrogen).

Further, as shown by Stefan (*loc. cit.*), when the diffusion medium is kept stationary during the steady flow of the vapour, the mass of the latter traversing the area A in period  $\Delta t$  is larger than  $\Delta m_1$  in the ratio  $1 + \frac{c_1}{c_2}$ : 1, where  $c_1$  and  $c_2$  are the concentrations of vapour and gas in the plane of the area. Thus

$$D_{12} \frac{c_2 + c_1}{c_2} \frac{\partial c_1}{\partial l} = \frac{1}{A} \frac{M_1}{t}, \quad \dots \dots (2)$$

where  $M_1$  denotes the mass of vapour crossing the area after time  $t$  from commencement of the steady flow and under the local gradient  $\frac{\partial c_1}{\partial l}$ .

It is an advantage of the conditions of the present investigation that  $c_1$  in the case of either vapour is so small compared with  $c_2$  in any region of the tube that the term  $\frac{c_2 + c_1}{c_2}$

may be considered as unity and the gradient  $\frac{\partial c_1}{\partial l}$  as constant.

The well-known complications in the general integration of equation (2) are avoided; and in this case

$$D_{12} \frac{C_1}{l} = \frac{1}{A} \frac{M_1}{t}, \quad \dots \dots (3)$$

where  $C_1$  is the saturation concentration of the given vapour,



and  $l$  the distance traversed by it from its source to the place of deposit. The errors in the values of  $D_{12}$  caused by this neglect of the quotient  $\frac{c_1}{c_2}$  range from 1 in 100,000 to 0.1 per cent. in the case of mercury, and from 0.1 per cent. to 1 per cent. in the case of iodine.

Ratios of the coefficients of diffusion through nitrogen of the two vapours are measured with extreme ease and accuracy by the present method, for the vapours diffuse simultaneously in the same tube at equal temperature and pressure. Ratios of this type must have importance, since they compare certain properties of the molecular species without reference to absolute molecular concentrations. Consider the two specific equations representing the diffusion in a single tube :

$$D_{\text{HgN}} \frac{C_{\text{Hg}}}{l} = \frac{1}{A} \frac{M_{\text{Hg}}}{t} \quad \dots \quad (3a)$$

and 
$$D_{\text{IN}} \frac{C_{\text{I}}}{l'} = \frac{1}{A'} \frac{M_{\text{I}}}{t'} \quad \dots \quad (3b)$$

When the tube is uniform,  $A = A'$ .

Since the period of steady flow starts and ends simultaneously at the two ends of the tube,  $t = t'$ .

Hence 
$$D_{\text{HgN}} \frac{C_{\text{Hg}}}{l} = D_{\text{IN}} \frac{C_{\text{I}}}{l'} \frac{M_{\text{Hg}}}{M_{\text{I}}} \quad \dots \quad (4)$$

It is found (*vide infra*) that the mercury and iodine are deposited in a nearly constant ratio by weight at a given temperature. That is, the salts composing the deposit are formed in a ratio apparently independent of the pressure of inert gas and of the dimensions of the tube. The ratio  $\frac{M_{\text{Hg}}}{M_{\text{I}}}$  in equation (4) has thus been assumed equal to, that is to say, extrapolated from, the values found in absolute determinations.

Equation (4) thus gives the required ratio  $\frac{D_{\text{HgN}}}{D_{\text{IN}}}$  from measurements of length and the vapour-pressures\* alone. Such relative determinations can be made under conditions of high nitrogen pressure or of low temperature which would render any absolute determinations difficult and slow.

\* Conversely, the method might be used for determining vapour-pressures from a knowledge of coefficients of diffusion together with two measurements of length.

The ratio  $\frac{D_{\text{HgN}}}{D_{\text{IN}}}$  as measured compares the diffusion of the two vapours under strictly similar conditions of gradient, even though the vapour-pressure of iodine greatly exceeds that of mercury. Under no circumstances could  $\dot{M}_{\text{Hg}}$  differ largely from  $\dot{M}_{\text{I}}$ , nor  $D_{\text{Hg}}$  from  $D_{\text{IN}}$  in a single tube, so that from (3)  $\frac{C_{\text{Hg}}}{l}$  and  $\frac{C_{\text{I}}}{l'}$  are of comparable magnitude. If under some hypothetical condition mercuric iodide were alone deposited, then  $\frac{\dot{M}_{\text{I}}}{\dot{M}_{\text{Hg}}} = 2$  in atomic units; if the mercurous salt were alone to appear,  $\dot{M}_{\text{I}}$  and  $\dot{M}_{\text{Hg}}$  would be atomic equivalents.

Owing to the large difference between the vapour-pressures of the two elements, the deposit occurs on the side of the tube close to the mercury and remote from the iodine. Measurement of the length traversed by the mercury is thus the more difficult. For more convenient measurement of this length, as is desirable in the case of the absolute measurements of diffusion, two alternative schemes are suggested, namely:—

- (1) A source of iodine vapour other than crystals of the free element, and such as to supply the vapour at a constant and suitably low pressure. The tri-iodide of caesium  $\text{CsI}_3$  would appear suitable from the investigation of this substance by Abegg and Hamburger (*Zeit. Anorg. Chem.* l. p. 403, 1906). It has not yet been used owing to the adoption of the second method.
- (2) Alternatively to constrict the tube along the region traversed by iodine vapour, and thus by diminishing  $A'$  on the right-hand side of equation:

$$D_{\text{HgN}} \frac{\partial C_{\text{Hg}}}{\partial l} \frac{A}{M_{\text{H}}} = D_{\text{IN}} \frac{\partial C_{\text{I}}}{\partial l'} \frac{A'}{M_{\text{I}}}$$

to cause the variable  $\frac{\partial C_{\text{Hg}}}{\partial l}$  to diminish on the left through an increase in the length traversed by mercury.

This device has been used for all the absolute measurements with mercury. Tubes so constricted are unsuitable for obtaining simultaneously values for iodine, because over the region of constriction the gradient  $\frac{\partial C_{\text{I}}}{\partial l'}$  must vary. It

would be difficult to trace the gradient from place to place directly.

Tubes of one metre total length are convenient. The constriction may take the form of a capillary, and should not offer so great a resistance as to make the deposit thin and indistinct, for increasing the distance traversed by the vapours has the effect of somewhat spreading out the deposit\*.

The design of the tube is important in another respect. The tube-walls must offer some resistance to the flow of the vapours, and this effect is superimposed upon the resistance of diffusion. The effect might be corrected for according to the laws of transpiration, but since it is small, even in the case of the narrowest tubes used, no correction has been applied.

For measurement of absolute values, a tube of 3-mm. bore is suitable, since this gives the greatest cross-section compatible with stability of the mercury meniscus at one end, or of an adherent sublimate of iodine at the other. A wide tube has the additional advantage of affording more deposit in a given time.

In relative determinations for which small deposits suffice, narrower tubes are preferable, since these give the better definition required for measurements of length. Capillaries of 1 mm. have been found best in this case.

Care must be taken to avoid contamination of either element by traces of the iodide deposit. In cases where the deposit forms in close proximity to the mercury, and especially in tubes of wide bore, there is a tendency for precipitation on the meniscus. Contamination in such cases is avoided by imparting a quivering motion to the meniscus, the tube being gently rocked. Rocking was performed in the vertical plane containing the axis of the tube, while care was taken that the end containing the mercury was always slightly the lower in level. In order that the rocking may be the more effective, there was a small gas space behind the mercury, for the tube was bent up in the form of a crook.

As regards the pressure of the gas, certain limitations must be observed. Since the rate of diffusion varies inversely as the pressure, it is necessary, for securing sufficient deposit in a reasonable time, to keep the pressure low. Especially in constricted tubes should the pressure be low, for in these the mercury has a greater distance to

\* In the limit resolving the deposit into *two* isolated bands. Details of this will be published later.

diffuse. But too low a pressure leads to spreading of the deposit by diffusion of its vapour, especially when the tube is wide. Pressures of 1 mm. to 10 mm. were used for the absolute values, and pressures up to 17 cm. for the relative values. For purposes in view it matters little what range of pressure is considered so long as the pressure is large in comparison with the partial pressures of the vapour, and yet low enough for the simple gas laws to hold.

A source of small error difficult to avoid is the mixing of the vapours and gas before the measurement of pressure  $P_N$ . The effect due to mercury is negligible. The iodine may increase the pressure by 0.1 mm., that is by about half the saturation pressure  $P_I$ , since its gradient extends along the tube. Further, after the final sealing, vaporization of the iodine must increase the partial pressure of nitrogen in the mercury end of the tube. Both kinds of effect are less for the constricted tubes, and in any case tend to cancel on the side of the tube containing mercury. They may together amount to 1 per cent. of the lowest pressures recorded, but were in all cases ignored.

In no case was more than 0.2 mg. of nitrogen contained in a tube. For economy therefore, also by reason of the stationary condition of the gas, the present method has advantages over those of Winkelmann and of Le Blanc and Wuppermann, each of which methods requires a continued circulation of many litres of gas, at constant pressure, throughout the period of experiment.

Owing both to the compactness of the tube and to the slowness of the process, there is no possibility of the cooling by vaporization pointed out by Le Blanc and Wuppermann.

## EXPERIMENTAL.

### (A) *Absolute Measurements.*

#### *Means of filling Diffusion Tube.*

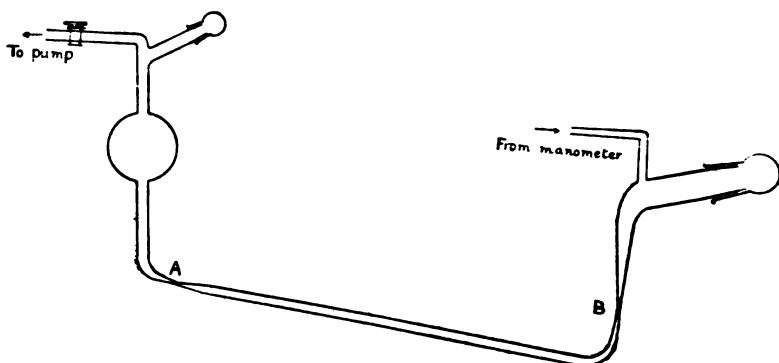
Fig. 2 shows the apparatus used. The diffusion tube, well cleaned, is sealed on at A and B and drawn down for convenient closing at these points. Iodine, of "AR" purity, is placed in the globe on the left side, while mercury—purified by electrolysis—is placed in a small iron boat in the sloping tube on the right-hand side. The iodine can be sublimed into the tube from the globe, and the mercury tipped in from the boat, an electromagnet being convenient for inverting the latter. No contamination is

thus incurred by grease or other surface film which would impede the vaporization.

Before introducing the mercury, the nitrogen is passed in and its pressure measured. The nitrogen was prepared from a commercial specimen of 99.7 per cent. purity containing very little argon. It was freed from oxygen by means of red-hot copper, and dried thoroughly. It is needless to enter into details of the purification. Traces of hydrogen were detected (derived from the heated copper), but the amount was negligible.

Exhaustion was effected by means of an oil-pump in such a sense as to cause the gas always to flow from the right-hand side to the left. This unidirectional flow is very

Fig. 2.



desirable in order to prevent iodine vapour from diffusing towards the mercury and contaminating the tube. The tube was heated to expel occluded gas and inevitable traces of mercuric iodide.

Iodine having been carefully sublimed into the tube, the pressure was measured at room temperature: high pressures on a manobarometer, and low pressures with a McLeod gauge. A correction (about 1 per cent. usually) was applied for the change in pressure due to transference to the higher temperature of the thermostat as described below.

Finally the mercury was introduced. This operation could not alter the pressure, owing to the large volume of the iodine globe.

The moment of the entrance of mercury may be taken as the starting time, since this almost coincides with the first appearance of deposit. The appearance of deposit does not mark the attainment of the steady state of flow, but this

state should not succeed it by more than an hour. Such a preliminary period is negligible in an experiment of ten days' duration. It will be remembered that in the experiments of Le Blanc and Wuppermann about one-tenth of the total time was allowed for at the start.

After sealing up, the tube was placed in a thermostat.

#### *Temperature of Experiment.*

Owing to the high temperature coefficients, both of vaporization and of diffusion, constancy of temperature is essential; yet the deposits are well defined when formed at room temperature. Convection in the tubes, then, is slight.

The temperature was throughout maintained at  $19^{\circ}\pm 4$  C. in a thermostat 4 feet long containing water circulated by four propellers. Except for one or two accidents the variation was about  $\pm 1/50^{\circ}$  C.

#### *The Measurements of Length.*

It is required to determine the length traversed by each vapour from its source to that part (or plane) of the deposit at which the concentration gradient first begins perceptibly to vary. As will be shown in a subsequent communication, the gradients of concentration do not change greatly at the outer fringe of the deposit, for chemical combination is restricted to a comparatively thin region or lamina in the centre portion of the deposit. Some of the visible spreading is due to diffusion of the saline vapours while in a state of supersaturation. These vapours and their dissociation products can in no way influence the normal gradients, since the dissociation constants are unchanged.

It is therefore necessary to measure the lengths up to the centre portion of the deposit; and since it is found that the two iodides fall alongside one another about a well-defined boundary, it is convenient to adopt this boundary as a mark for the measurements of length.

It is found that there is a distinct ridge of the red crystals alongside and close to the boundary. The deposit is thickest in the plane of this ridge at the temperature investigated. Since, however, we do not necessarily seek the planes across the deposit which contain the centres of gravity of the elements deposited, the presence of this ridge has been ignored in taking the measurements of length. Discussion of the detailed features of the deposit must be deferred to a future occasion.

At the ends of the tube imaginary planes must be found from which diffusion may be assumed to commence. The mercury meniscus is a segment of a sphere. The plane cutting this segment parallel to its base and through a point bisecting its height will therefore divide the vaporizing surface into equal areas. Since these areas are nearly equidistant from the deposit, it is safe to consider this place as the effective source of vapour. After locating the base of the meniscus, a correction was thus applied for half its height. Contraction of the mercury column on removal from the thermostat was allowed for; to obviate this source of error and to diminish the risk of derangement caused by handling, an endeavour will later be made to read the lengths while the tube remains in the thermostat.

Measurements were made with the tube in four positions about its axis, the asymmetry of a meniscus in horizontal tubes being taken into account.

The short distance traversed by mercury vapour can thus be read with an accuracy of about 0.05 mm. or  $\pm 0.5$  per cent.

Definition of the iodine is secured by careful filling of the tube. Observation must be made of the slight retreat along the tube during the period of consumption. On a length of 1 metre an accuracy of  $\pm 0.2$  per cent. is certain.

After measurement the tube is opened by cutting it beside the deposit; simultaneously the period of diffusion is considered at an end.

#### *Analysis of the Deposit.*

The iodine has been determined directly, the mercury by difference.

Weighings have been conducted with great accuracy through the kindness of Mr. A. C. Egerton, whose balance has been used. The authors take this opportunity of cordially thanking him for his interest in the work.

The weighed deposit is dissolved in 10 c.c. of hydrochloric acid of 5 N strength containing 2 c.c. of 0.1 N nitric acid, Kjeldahl's apparatus being used to prevent escape of iodine. Solution is slow even when conducted in a steam bath. As the mercuric iodide dissolves the more rapidly, it can be seen how sharp is the boundary towards the other salt. When solution is complete, 2 or 3 c.c. of 0.1 N sodium sulphite are added to reduce iodate, and the mixture left to stand. The mixture then contains no mercurous compounds, and the iodine as  $I^-$  ions.

The method of Fresenius ('Quant. Chemical Analysis,' vol. i. 7th ed. p. 366) was used to estimate this iodine, chloroform being used for its isolation. A deposit of

0.04 gram gives but one titration of 15 c.c. with  $\frac{N}{100}$  sodium thiosulphate, but there is little danger of an overshoot, since several of the chloroform extractions are needed for withdrawal of the iodine.

#### Cross-section of the Tube.

Short lengths from the region traversed by mercury were measured by optical examination of the cut ends, while long lengths from the iodine side were filled with mercury at the temperature of diffusion and weighed.

Commercial tubing was used, which was found sometimes to vary as much as 5 per cent. along its length. Mean values as determined cannot, however, be greatly in error.

#### Numerical Values.

It would be tedious to tabulate all the measurements made, since one experiment of each type will illustrate the magnitudes concerned.

Thus in an experiment upon iodine :—

Temperature of thermostat .....	19.40° C.
Pressure at room temperature .....	9.616 mm. of Hg.
" ( $P_N$ ) reduced to 19° 4 .....	9.78       "
Length from iodine to deposit when first formed...	892.5 mm.
Retreat of iodine .....	2.0       "
Corrected length ( $l'$ ) .....	891.5       "
Time-interval ( $t$ ) 12 days, 1 hr., 17 mins.	
Mass of iodine deposited ( $M_I$ ) .....	0.01163 gram.
Mean cross-section of tube at 19.4° C. ( $A'$ ) .....	6.472 mm. <sup>2</sup>

$$\text{Therefore } D_{IN} = 5.80 \text{ cm.}^2 \text{ sec.}^{-1}$$

In one for mercury at the same temperature :—

Pressure at room temperature .....	5.608 mm. of Hg.
" ( $P_N$ ) reduced to 19° 4 .....	5.65       "
Length from base of meniscus to deposit being a mean of 4 readings .....	20.85 mm.
Meniscus correction .....	0.50       "
Corrected length ( $l$ ) .....	20.35       "
Time-interval ( $t$ ) 20 days, 22 hrs., 12 mins.	
Mass of whole deposit .....	0.02474 gram.
" iodine.....	0.01129       "
" mercury by difference ( $M_{Hg}$ ) .....	0.01344       "
Cross section of tube over region traversed by mercury ( $A$ ) .....	6.630 mm. <sup>2</sup>

$$\text{Therefore } D_{HgN} = 17.3 \text{ cm.}^2 \text{ sec.}^{-1}$$

Constriction of tube required in this experiment = 45 cm. length of 1 mm. capillary.



*Iodine-Nitrogen at 19°·4\*.*

Pressure of nitrogen, mm.	$D_{IN}$ cm. <sup>2</sup> sec. <sup>-1</sup> .	$\frac{1}{P_N + \frac{1}{2}P_I}$	$D_{IN}(P_N + \frac{1}{2}P_I)$	Remarks.
13·7	3·99	0·0725	55·03	Preliminary experiment value low.
6·61	8·46	0·1492	56·71	Pressure doubtful.
9·52	6·05	0·1040	58·17	
7·5	7·63	0·1318	57·89	Air-leak into manometer roughly corrected for.
9·85	5·84	0·1006	58·05	
9·83	5·70	0·1008	56·55	
9·78	5·80	0·1013	57·25	Reliable.
9·27	6·33	0·1068	59·27	Cross-section uncertain; tube broken.
9·71	5·81	0·1020	56·96	Reliable.

Weighted mean..... 57·0

\* Assumed  $C_I = 2·623 \times 10^{-6}$  gram per c.c., corresponding to  
 $P_I = 1·884 \times 10^{-1}$  mm.

*Mercury-Nitrogen at 19°·4†.*

Pressure of nitrogen, mm.	$D_{HgN}$ cm. <sup>2</sup> sec. <sup>-1</sup> .	$\frac{1}{P_N + \frac{1}{2}P_{Hg}}$	$D_{HgN}(P_N + \frac{1}{2}P_{Hg})$	Remarks.
5·65	17·3	0·1770	97·04	
2·55	>34·0	0·3921	>86·72	D value low tube not rocked.
2·45	39·6	0·4080	97·06	Deposit not well defined.
3·52	27·2	0·2840	95·77	Reliable.
1·97	49·5	0·5075	97·53	
3·40	27·3	0·2941	92·84	Air-leak.

Weighted mean..... 97·0

† Assumed  $C_{Hg} = 1·32 \times 10^{-6}$  gram per c.c., corresponding to  
 $P_{Hg} = 1·20 \times 10^{-3}$  mm.

$$\text{Hence the ratio } \frac{D_{HgN}}{D_{IN}} = \frac{97}{57} = 1·70$$

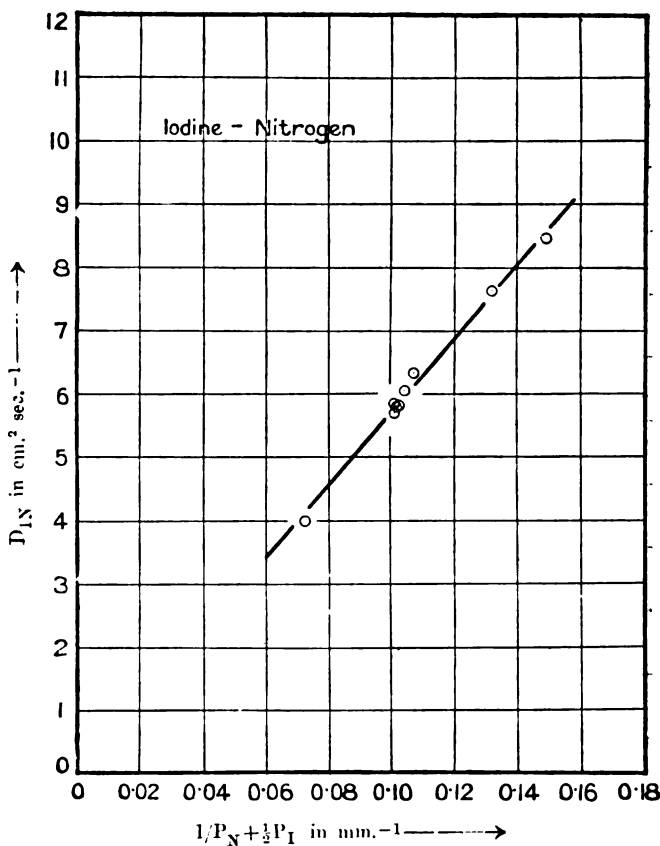
It is clear that the figures in the fourth column are in each case nearly constant.

In figs. 3 and 4 the diffusion coefficients are plotted against the reciprocals of the total pressures.  $P_{Hg}$  and  $P_I$  denote the saturation pressures of the vapours, so that  $\frac{1}{2}P_{Hg}$  and  $\frac{1}{2}P_I$  should represent the mean partial pressures along the regions of diffusion.

The coefficients for mercury are practically as concordant as those for iodine, but would be subject to a greater

constant error if the adopted boundary were unsuitable for the measurement of length.

Fig. 3.



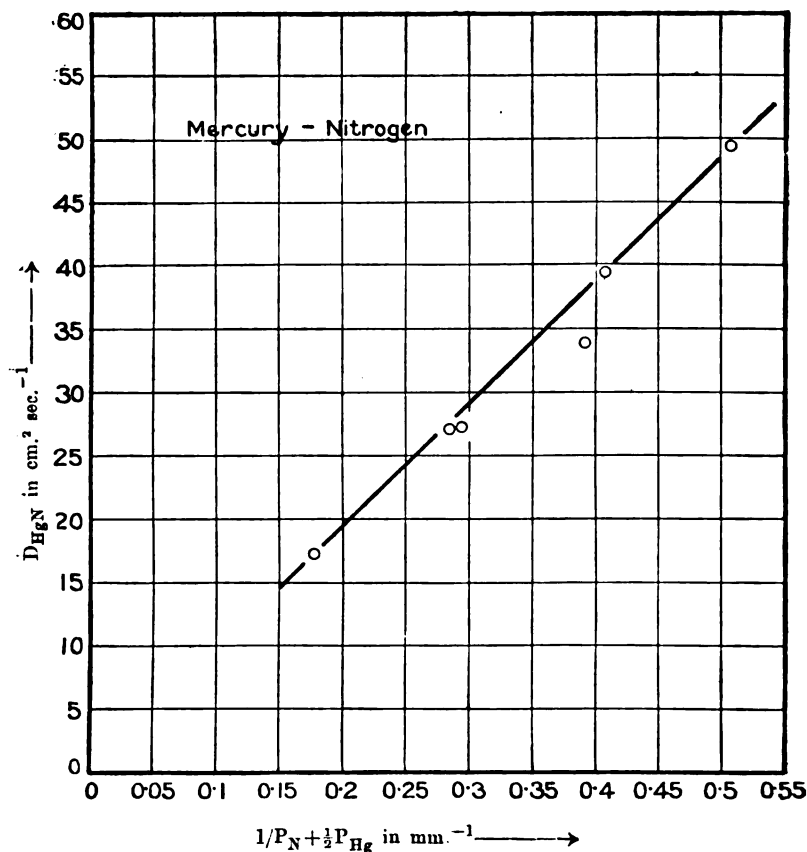
### (B) Relative Measurements.

The relative determinations are much simpler, since they need not involve estimates of time or those of tube section, or even those of mass.

From the analysis of the deposits it has been found that the two elements are precipitated in a nearly constant ratio by weight at the given temperature. That this is so can be easily imagined, for in the hypothetical case where the amount of nitrogen is infinitely small, the rates of deposition.

of the iodides would be determined solely by their dissociation pressures. (The co-precipitation of two electrolytes which possess an ion in common is closely analogous, but comparison must for the present be postponed.) The presence of the inert gas nitrogen could modify this

Fig. 4.



condition only by hindering the approach of the iodide vapours to the walls of the tube, the ratio of masses deposited being thus dependent upon the diffusivities of the iodides and of their dissociation products as well as upon their equilibrium pressures. When the diffusion effect is small, as in narrow tubes, the ratio of masses deposited must

at a given temperature be nearly independent of the total pressure. The following table shows the values found :—

Ratio of masses deposited, Hg/l.	Pressure of nitrogen. mm.
1·108	7·5
1·114	9·85
1·189	5·65
1·187	9·78
1·144	9·27
1·187	9·71
1·205	2·55
1·203	2·45
1·161	3·52
1·129	1·97
ca. 1·100	3·40

Average... 1·16

The ratio of masses deposited is thus nearly constant under the conditions of experiment \*.

Since this ratio is constant (at the temperature considered), it is requisite from equation (4) that the ratio of lengths  $\frac{l''}{l}$  be likewise constant under the given conditions. The constancy of the ratio  $\frac{l''}{l}$  is very rigorously shown by experience (see table below); indeed, the accuracy attainable in the measurement of length exceeds that of the chemical analysis, and affords a very real check on the uniformity of the process. The ratio of masses is uninfluenced by a constriction in either end of the tube, because this is in effect merely a lengthening of the tube, and not an alteration of the ratio  $\frac{l''}{l}$  (analogous to a resistance in an arm of Wheatstone's electrical bridge).

For the relative determinations of diffusion the ratio of masses deposited has been assumed the same as in absolute determinations, while the lengths have been measured. To correct for the inevitable tapering of the tube, the measured ratio of lengths  $\frac{l''}{l}$  must be divided by the ratio of the mean sections  $\frac{A'}{A}$  along the corresponding regions of diffusion.

\* The irregularities have subsequently been found to be due to a slow photo-chemical action of mercurous iodide. These irregularities can obviously not effect the accuracy of the absolute measurements of diffusion.

The following is a typical experiment :—

Pressure at 19·4 .....	179·0 mm. of Hg.
Length from base of meniscus to deposit (4 readings).....	6·09 mm.
Meniscus correction .....	0·13 „
Correction for temperature of reading .....	0·01 „
Mercury length corrected ( $l$ ).....	5·95 „
Iodine length ( $l'$ ) .....	761·5 „
Therefore ratio of lengths observed ( $\frac{l'}{l}$ ).....	128·1
Mean tube diameter... ..	1·18 mm.
Ratio of mean cross-sections along the two regions of diffusion ( $\frac{A}{A'}$ ).....	1·015
Therefore ratio of lengths for a uniform tube ( $\frac{l'}{l} \times \frac{A}{A'}$ ) = 128·1 × 1·015	= 130·0
Assumed ratio of masses deposited $\frac{M_{\text{Hg}}}{M_{\text{I}}}$ .....	= 1·16
Therefore $\frac{D_{\text{HgN}}}{D_{\text{IN}}}$ at 19°·4 .....	= 1·77

The table gives the ratios determined at 19° 4.

Tube.	Pressure total. mm.	Ratio of lengths for a uniform tube.	$\frac{D_{\text{HgN}}}{D_{\text{IN}}}$ .	Remarks.
A.....	102	128·4	1·79	Preliminary experiment.
B.....	179·0	130·0	1·77	Reliable.
B again ...	„	128·8	1·78	
C.....	72·0	128·6	1·79	Pressure uncertain; iodine badly placed.
C again ...	„	127·5	1·80	
D .....	67·5	128·7	1·79	Ill-defined deposit.
D again ...	„	133·7	1·72	
E.....	79·0	128·9	1·78	Narrow tube difficult to fill; values reliable.
E again ...	„	130·0	1·77	
Average .....			1·78	

Such experiments were repeated in the case of most tubes. The tube was reset by shaking the mercury a little further along the axis so as to produce a new deposit on the clear wall. The second deposit was usually better defined than the first, owing to microscopic crystal nuclei previously spread about, and because of the quickness of re-attainment of a steady state.

It should be observed that the application of the method to relative measurements of diffusion rests upon facts additional to those which fit the method for absolute measurements. Absolute measurements could be made whether

or not the deposit is of regular constitution, provided only it occurs in a very limited region of the tube, for equation (1) is quite determinate, as is well known, and for integration requires solely a knowledge of the distribution of concentration. The relative measurements are rendered simple, not only by the simultaneous presence of the two vapours, but by the regularity of the deposits which permits extra-

polation of the ratio  $\frac{M_{Hg}}{M_I}$ . The corresponding ratio in the

case of similar diffusion of ammonia and hydrogen chloride would be fixed stoichiometrically, since only one salt, ammonium chloride, is then possible.

The average ratio 1.78 of the coefficients of diffusion differs but slightly from the value 1.70 obtained from the absolute determinations at low pressures. The difference is probably real, since the coefficients of diffusion may vary with the proportions in which vapour and gas are mixed. But no great stress is laid upon this difference, since it is comparable with the errors of experiment. The difference

is due partly to the neglect of the term  $\frac{c_1}{c_2}$  in Stefan's equation (2) (meaning that 1.70 is too small a ratio), and partly to resistance offered by the narrow tubes to the flow of iodine vapour (1.78 being thus too large).

The magnitude of the mean ratio 1.74 shows that iodine diffuses more slowly than does mercury.

Interpolation from the direct observations gives for a temperature of 19°.4 C.:

$$D_{HgN} = 32.3 \text{ when } P_N + \frac{1}{2}P_{Hg} = 3.00 \text{ mm.}$$

$$\text{and } \frac{P_N}{\frac{1}{2}P_{Hg}} = 5.0 \times 10^3,$$

$$\text{and } D_{IN} = 5.70 \text{ when } P_N + \frac{1}{2}P_I = 10.00 \text{ mm.}$$

$$\text{and } \frac{P_N}{\frac{1}{2}P_I} = 1.06 \times 10^2.$$

Discussion of these results must be postponed to a future communication.

The authors desire to express their best thanks to Professor Lindemann for his valuable advice, to Mr. A. C. Egerton, and to General H. B. Hartley of Balliol College;

*Phil. Mag.* S. 6. Vol. 48. No. 288. Dec. 1924. 4 E

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also to Mr. I. O. Griffith. They acknowledge their indebtedness to the Chemical Society for a grant which has partly defrayed the cost of the investigation.

14 Bardwell Road,  
Oxford.  
September 1924.

[*Note added November 8th.*—A fact which further simplifies the method is that both ends of the diffusion tube may be left open to a pure atmosphere of the inert gas. No stream of the gas traverses the tube once the steady state is established, for gradients of the vapours are set up from the elements towards the open ends, and the pressure of inert gas is the same at these ends. In some experiments upon diffusion through air it has been found easy to shake the elements out of an open tube and rearrange at will.—J. M. M.]

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(IX. *Pole Lines occurring in the Interrupted Arc Spectra of Silver, Gold, and Copper.* By H. LOWERY, M.Sc. (Lond.), A.Inst.P., F.R.A.S., Assistant Lecturer in Physics, Manchester University\*.

[Plate XXVII.]

**D**URING the course of an investigation on the Stark effect in the arc, the spectra of "arc flashes" between silver, gold, and copper poles in air, hydrogen, and oxygen were photographed. Of the many interesting points exhibited by the photographs, it is proposed in this paper to refer to certain lines which seem to be associated with the lower pole of the arc under the particular conditions of the experiments.

#### EXPERIMENTAL DETAILS.

The method of making an arc flash was that used by Hemsalech and the Comte de Gramont†. The lower pole was kept fixed throughout the experiments whilst the upper pole was arranged so that by pulling a cord it could be drawn into contact with the lower pole. When the poles came into contact, the circuit was made through a key and the cord released. An arc was thus formed between the poles, but the upper pole was caused to move away quickly

\* Communicated by Prof. W. L. Bragg, F.R.S.

† Phil. Mag. vol. xliii. (Feb. and May 1922).

from the lower pole to such a distance that the arc ceased to pass, so that only an arc flash was produced.

It will be convenient to speak of the arc observed in this manner as the *interrupted* arc to distinguish it from the *continuously-burning* arc.

Experiments were made under various electrical conditions and the voltage and current at contact of the poles were recorded. The voltages were varied from 100 to 400 volts and the currents when the circuit was made ranged from 0.3 to 25 amperes. Of course the intensity of the arc flashes changed considerably with these wide differences in voltage and current, thus necessitating more flashes for a photographic exposure in some of the experiments than in others. The lower pole was usually negative in the experiments, though for special tests it was made positive.

#### THE SPECTROGRAPH.

For the purpose of this research a spectrograph was mounted in which a small Rowland grating (14,438 lines to the inch; radius of curvature 72 in.; ruled space 2 in. long) was used with a 3 in. refracting telescope as collimator. The eyepiece of the telescope was replaced by a Hilger slit which was adjusted to be at the focus of the objective so that the rays leaving the objective after passing through the collimator were parallel. The grating and camera were mounted on the same support, which turned about a point in the axis of the collimator vertically under the grating.

It will be observed that in this mounting, since parallel light is allowed to fall on the concave grating, stigmatic images of the light source are produced.

The dispersion given by the spectrograph in the first order was about 19 Å.U. per mm.

#### EXPERIMENTAL RESULTS.

Before an experiment was begun, care was taken to focus the lower fixed pole of the arc just below the middle of the collimator slit and to arrange that each arc flash should fall along the length of the slit. The object in conducting the experiments in this manner was to obtain photographs of the spectra due to the earliest stages in the formation of a flash. Since the particular mounting of the grating employed gave stigmatic images, the effects introduced into the spectra during the initial stages of an arc flash were readily distinguished.



TABLE I. Pole Lines (Silver).

Wave-lengths in I.A.	Class.	Intensity.	Previous Observer.
3560.5 (a)	I	2	.....
3576.2	II	1	.....
3580.62	I	1	Eder and Valenta *: Spark.
3630.09 (b)	I	1	Frings †: Spark.
3630.6 (c)	II	1	.....
3649.82	I	2	Eder and Valenta: Spark.
3683.25	I	3	" " "
3728.2	I	2	.....
3766.35	I	1	Exner and Haschek ‡: Arc.
3829.3	I	1	.....
3840.80	I	3	Frings: Arc.
3877.25	I	1	Exner and Haschek: Spark.
3907.48	I	4	Kayser and Runge §: Arc.
3914.32	I	4	" " "
3920.10	I	2	Wagner   : Spark.
3945.6	II	1	.....
3985.03	I	2	Eder and Valenta: Spark.
4004.75	I	1	Exner and Haschek: Spark.
4012.3 (d)	II	1	.....
4063.6	I	1	.....
4068.01	I	3	Frings: Spark.
4081.7 (e)	I	0	Takamine ¶.
4085.90	I	1	Frings: Spark.
4141.6	II	1	.....
4182.1	II	1	.....
4206.8 (f)	I	0	Takamine.
4226.55 (g)	I	1	"
4281.2	II	1	.....
4298.1	I	1	.....
4381.4	II	1	.....
4395.94	I	2	Frings: Spark.
4455.4	I	1	.....
4548.9	I	1	.....
4550.4	I	1	.....
4610.6	I	1	.....
4614.5	II	1	.....
4615.82	I	2	Eder and Valenta: Spark.
4620.39	I	0	" " "
4650.3	I	1	.....
4657.2	I	1	.....
4677.86	I	2	Kayser and Runge: Arc.
4680.4	I	1	.....
4721.1	I	1	.....
4785.5	II	1	.....
4811.3	I	3	.....
4843.3	I	1	.....
4870.2	I	3	.....
4934.3	II	1	.....

\* 'Atlas Typischer Spektren' (Wien, 1911).

† *Zeit. für wiss. Phot.* xv. p. 165 (1915).

‡ Tabellen der Funkenlinien (1902); Tabellen der Bogenlinien (1904).

§ Handbuch der Spectroscopie, Band V. (Leipzig, 1910).

|| Dissertation (Bonn, 1911).

¶ Astrophys. Journ. vol. 1. (1919).

*Notes on Table I. (Silver).*

(a)  $\lambda$  3560.5 and (d)  $\lambda$  4012.3.—At the beginning of the arc flash both lines are displaced to the red from their positions during the later stages, (a) by about 1 Å.U. and (d) by about 0.5 Å.U.

(b)  $\lambda$  3630.09 and (c)  $\lambda$  3630.6.—The latter line (not previously recorded) is displaced to the red by about 0.5 Å.U. at the making of the arc. The displacement is readily detected owing to the nearness of  $\lambda$  3630.09.

(e)  $\lambda$  4081.7, (f)  $\lambda$  4206.8, and (g)  $\lambda$  4226.55.—The wave-lengths of these three lines are as recorded by Takamine who, in his research on the Stark effect for silver\*, records that the lines (e) and (g) only occur in a strong electric field. In the present work, all three lines are confined to the initial stages of the arc flash. In the experiments with heavy currents, the line  $\lambda$  4206.8 is usually masked by a wing which accompanies the arc line  $\lambda$  4210 on the violet side at the beginning of a flash.

Whether the interrupted arcs between silver, gold, and copper poles were made in air, hydrogen, or oxygen, the corresponding photographs are characterized by a number of lines which appear only during the early stages of an arc flash. These lines seem to be closely associated with the lower fixed pole and occur whether that pole is positive or negative, though they are certainly more numerous under the latter condition. For convenience, they will be termed *pole lines*: they are presumably lines which are specially enhanced under the abnormal conditions of voltage and current employed, and are possibly due to the excitation of multiply ionized atoms.

A careful study of these pole lines reveals the fact that they may be arranged into two classes as follows:—

*Class I.*

Whereas the ordinary arc lines cease when the poles are about 6 mm. apart, the lines of this class commence with moderate intensity and decrease gradually in intensity till they disappear when the poles are separated by about 1 to 3 mm., though the actual distance of separation of the poles at which disappearance takes place seems to depend (between the above limits) upon the value of the initial current.

*Class II.*

Lines comprised in this class come to an end abruptly when the poles are about 1 mm. apart. They are of uniform intensity along their lengths, and changes in the initial currents affect only their intensities and not their lengths. Their intensities seem also to depend on the voltages employed, for the lines are much stronger at 350 volts than

\* *Loc. cit.* p. 26.

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at 250 or 110 volts. There are 11 lines of Class II in the interrupted silver arc spectrum, 6 in the gold and 2 in the copper in the region,  $\lambda$  5220 to  $\lambda$  3380, covered by the research.

TABLE II. Pole Lines (Gold).

Wave-lengths in Å.	Class.	Intensity.	Previous Observer.
3649.10	I	4	Eder and Valenta: Spark.
3706.84	I	2	" " "
3950.04	I	1	" " "
3959.20	I	4	" " "
3968.7	I	5	.....
3985.89	I	2	Eder and Valenta: Spark.
3989.85	I	1	" " "
3991.49	I	3	" " "
3994.1	II	2	.....
4012.72	I	4	Eder and Valenta: Spark.
4027.3	II	1	.....
4028.51	I	1	Eder and Valenta: Spark.
4061.05	I	2	Exner and Haschek: Spark.
4070.61	I	3	Eder and Valenta: Spark.
4076.45	I	5	" " "
4089.80	I	2	" " "
4171.26	I	2	" " "
4171.9 (a)	II	2	.....
4172.74	I	2	Eder and Valenta: Spark.
4227.3	I	1	.....
4229.2	I	1	.....
4260.5 (b)	I	2	.....
4275.84	I	1	Eder and Valenta: Spark.
4361.2	II	2	.....
4395.55	I	1	Eder and Valenta: Spark.
4467.3	II	1	.....
4558.87	I	1	Eder and Valenta: Spark.
4597.2	II	1	.....
4599.4 (c)	I	1	.....
4630.40	I	2	Eder and Valenta: Spark.
4633.05	I	1	" " "
4640.54	I	0	" " "
4643.08	I	1	" " "
4673.06	I	1	" " "
4902.27	I	2	" " "
4920.32	I	1	" " "

*Notes on Table II. (Gold).*

(a)  $\lambda$  4171.9 (not previously recorded) is readily observed between the spark lines  $\lambda$  4171.26 and  $\lambda$  4172.74, from which it is quite separate.

(b)  $\lambda$  4260.5 (not previously recorded) is easily distinguished from the spark line 4259.85 (intensity 1).

(c)  $\lambda$  4599.4 usually disappears when the poles are about 2 mm. apart and is displaced to the red by 1 Å. U. at the beginning of the arc flash.

The lines of the second class do not occur in the continuously-burning arc spectra, though a few of the stronger lines of the first class appear in the neighbourhood of each pole under these conditions, being more pronounced at the negative than at the positive pole. The same lines of each class appear in the spectra of the interrupted arcs whether the arcs are made in air, hydrogen, or oxygen; but, for given electrical conditions, they are slightly more intense when the arc flashes are made in hydrogen than when they are made in air and oxygen (when the intensities are nearly equal).

It is to be particularly noted that most, though not all, of the lines of the first class have been identified with lines observed by previous experimenters in the arc or spark spectra of the respective metals, whereas the lines of the second class do not seem to have been previously recorded.

Tables I., II., and III. contain lists of the pole lines of

TABLE III. Pole Lines (Copper).

Wave-lengths in I. Å.	Class.	Intensity.	Previous Observer.
3539.1 (a)	II ?	0	.....
3595.3	II	1	.....
3597.8 (b)	II	2	.....
3641.693	I	3	Hasbach * : Arc.
3654.3 (c)	I	6	" "
3684.925	I	1	" "
3697.84	I	2	Eder and Valenta : Spark.
3700.41	I	2	" " "
3737.47	I	1	" " "
3764.75 (d)	I	2	Kayser and Runge : Arc.
3777.02	I	4	Eder and Valenta : Spark.
3790.97	I	2	" " "
3807.69	I	3	" " "
4015.8	I	1	Hasbach : Arc.
4056.7	I	4	" "
4227.93	I	3	" Spark.
4683.17	I	2	Eder and Valenta : Spark.
4758.578	I	2	Aretz † : Spark.
4813.9	I	2	Hemsalech ‡.
4910.325	I	3	Aretz : Spark.

\* *Zeit. für wiss. Phot.* xiii. p. 399 (1914).

† Dissertation (Bonn, 1911).

‡ 'Spectres d'Étincelles' (Paris, 1901).

*Notes on Table III. (Copper).*

(a)  $\lambda$  3539.1 is very feeble in all the photographs and it is not possible to say definitely whether it belongs to Class I. or to Class II.

(b)  $\lambda$  3597.8 (not previously recorded) and (d)  $\lambda$  3764.75 are both displaced to the red by 1 Å.U. at the beginning of the arc flash.

(c)  $\lambda$  3654.3 is displaced to the red at the making of the arc, actually coinciding with the line  $\lambda$  3655.84.

both classes occurring in the interrupted arc spectra of silver, gold, and copper respectively in the region  $\lambda$  5220 to  $\lambda$  3380 when the initial current was 5 amperes and 350 volts were across the poles at contact (the lower pole being negative). In recording the intensities of the lines, the scale adopted ranged from 0 to 10, the former representing the weakest and the latter the strongest lines in the spectra. The intensities given for the lines of Class I are those at the beginning of the arc flash.

As pointed out by Hemsalech and the Comte de Gramont\* in the interpretation of the results of their experiments with the interrupted arc, one of the many possible effects introduced into the resulting spectra is that due to the strong electric fields set up when the upper pole is just beginning to separate from the lower. In this connexion, the behaviour of the lines  $\lambda\lambda$ 4081.7, 4226.55 (silver), and  $\lambda\lambda$ 4015.8, 4056.7 (copper) under the interrupted arc conditions is interesting. These four lines occur only at the beginning of an arc flash, which would be expected since, according to Takamine †, they occur only in a strong electric field.

It may be noted here that a classification of spectral lines similar to that above was found by Milner ‡ during the course of an examination of the streamers in the electric spark. In view of the "high tension" conditions which must exist between the poles of the arc during the early stages of the flash, it seems likely that the pole lines of the present work are closely allied to the "condensed-spark" lines of Milner's classification.

*"New" lines occurring in the interrupted arc spectra.*

The following pole lines (Table IV.) appearing in the interrupted arc spectra of silver, gold, and copper have not been identified in the lists of arc and spark lines given by previous observers. The roman numerals refer to the classification of pole lines already described.

Catalan § gives a list of 98 new lines in the arc spectrum of silver in the region  $\lambda$  4500 to  $\lambda$  2300. He also gives a comparison table which shows that, with 10 exceptions, these "new" lines have wave-lengths which agree very closely with lines given by Eder and Valenta as occurring in the spark.

\* *Loc. cit.* p. 306 and p. 848.

† *Loc. cit.* p. 30.

‡ *Proc. Roy. Soc. A*, lxxxi, p. 299 (1908).

§ "Nuevas Líneas en el Espectro de Arco de la Plata entre 4500 y 2300 U.A." M. A. Catalan, *An. de la Soc. de Fís. y Quím.* xv, p. 483 (1917).

TABLE IV.

SILVER.			GOLD.			COPPER.		
Wave-length in I.A.		Intensity.	Wave-length in I.A.		Intensity.	Wave-length in I.A.		Intensity.
3560.5	I	2	3968.7	I	5	3539.1	II?	0
3576.2	II	1	3994.1	II	2	3595.3	II	1
3630.6	II	1	4027.3	II	1	3597.8	II	2
3723.2	I	2	4171.9	II	2			
3829.3	I	1	4227.3	I	1			
3945.6	II	1	4229.2	I	1			
4012.3	II	1	4260.5	I	2			
4063.6	I	1	4361.2	II	2			
4141.6	II	1	4467.3	II	1			
4182.1	II	1	4597.2	II	1			
4281.2	II	1	4599.4	I	1			
4298.1	I	1						
4381.4	II	1						
4455.4	I	1						
4548.9	I	1						
4550.4	I	1						
4610.6	I	1						
4614.5	II	1						
4650.3	I	1						
4657.2	I	1						
4680.4	I	1						
4721.1	I	1						
4785.5	II	1						
4811.3	I	3						
4843.3	I	1						
4870.2	I	3						
4934.3	II	1						

Unfortunately, only the region  $\lambda 4500$  to  $\lambda 3380$  of Catalan's work is included in that of the present investigation. However, all the lines within this region which Catalan was able to identify with spark lines are developed in the interrupted arc spectrum of silver, most of them passing through all the stages of the arc flash.

Of the 10 lines mentioned above which Catalan failed to identify, 9 fall within the region of the present work, but none of them appear in the interrupted arc spectrum. It is important to note that Catalan's list of new lines in the arc spectrum of silver does not include any of the unidentified pole lines occurring in the spectrum of the interrupted arc between silver poles.

Duffield \*, in his study of the effect of pressure on the arc spectrum of *gold*, found a large number of lines not

\* Phil. Trans. A, ccxi. p. 51 (1911).

### 1130 *Pole Lines occurring in Interrupted Arc Spectra.*

chronicled by Kayser and Runge. However, there is no agreement between the above unidentified pole lines and the lines given in Duffield's list for gold except possibly in the case of  $\lambda 4467.3$  (II). This may be the line  $\lambda 4466.25$  which Duffield failed to identify.

In the spectrum of the steadily-burning *silver* arc under pressures of at least 20 atmospheres, Duffield \* records that the ordinary line spectrum was replaced by a number of bands. It is possible that of these bands, those at  $\lambda 4062.9$  and  $\lambda 4298.0$  (at 25 atmospheres pressure) have some connexion with the unidentified pole lines  $\lambda 4063.6$  (I) and  $\lambda 4298.1$  (I).

The unidentified copper pole lines occurring in the present work fall outside the region of Duffield's research.

#### *Explanation of Plate.*

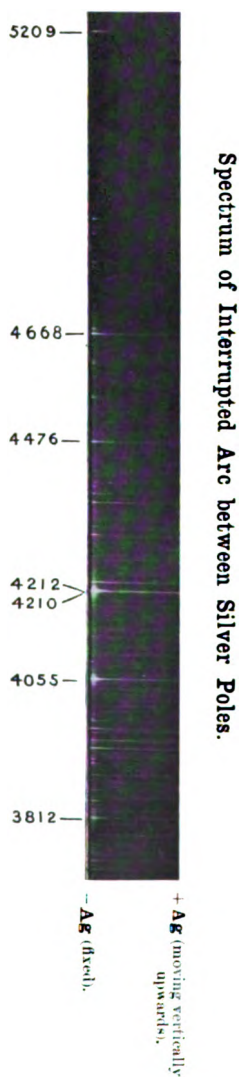
The photograph is reproduced from one of the negatives obtained when arc flashes were made between silver poles in oxygen at 350 volts and initial current  $2\frac{1}{2}$  amperes, the lower pole being negative. Although the distinction between the two classes of pole lines is not readily brought out, the photograph illustrates the general appearance of the pole lines and shows how they are associated with the lower fixed pole.

It will be noticed that many of the spectral lines are widened in the immediate vicinity of the lower pole. The widening is particularly noticeable in the lines  $\lambda\lambda 4055, 4210$ , and is probably a manifestation of the Stark effect †. Throughout the experiments it was frequently noticed that when the widening was most evident, the pole lines were developed with the greatest intensity.

The line  $\lambda 4055$  differs from all the other widened silver lines in that it is accompanied by a component on the violet side during the early stages of the arc flash. With comparatively short photographic exposures, this component is of sufficient intensity to be plainly visible in the presence of the wing on the same side of the line. The component is at its maximum distance (about 2 Å.U.) from the principal line when the upper pole just commences to leave the lower, and the distance between the two lines decreases gradually until the component finally meets the principal line when the poles are  $\frac{1}{2}$  to 1 mm. apart according to the voltage employed.

\* *Loc. cit.* p. 43.

† Hemsalech and the Comte de Gramont, *loc. cit.*







SUMMARY.

1. Results are given of spectroscopic observations of the silver, gold, and copper arcs produced under conditions similar to those of Hemsalech and the Comte de Gramont.

2. In the region studied,  $\lambda$  5220 to  $\lambda$  3380, a number of lines have been found in the neighbourhood of the fixed pole which readily fall into two classes according as they cease abruptly at the end of the initial stages of the arc flash or tend to pass on into the intermediate and final stages.

3. Most of the lines have been identified with previously observed arc and spark lines, but a number of them do not seem to have been previously recorded.

4. Lists of the "new" lines occurring in the region  $\lambda$  5220 to  $\lambda$  3380 of the spectra of the interrupted arcs between silver, gold, and copper poles are given.

In conclusion, I desire to express my thanks to Dr. G. A. Hemsalech for suggesting the original research, for his assistance in mounting the apparatus, and for his helpful advice and criticism while the experiments were in progress. My thanks are also due to Professor W. L. Bragg, M.A., F.R.S., who has given me every facility for carrying out the investigation and has shown much interest in the development of the results.

Physics Dept.,  
The University of Manchester,  
July 1924.

CX. *Notices respecting New Books.*

*Relativity for Physics Students.* By Prof. G. B. JEFFERY.  
Methuen. 6s. net.

OF the torrent of books on relativity, written for audiences of many types, from the man in the street to the scientific specialist, we would certainly select the present volume as being in some ways novel and valuable. The author has directed his attention to the growing body of young physicists who have neither the time nor the inclination to become really expert mathematicians, but who prefer to pursue their studies of physics while preserving mathematics as a useful key to unlock doors when they are found to be shut. He has succeeded in a notable way, in giving a most readable and logical account of all the essentials of the theory, without the usual excursions into the labyrinths of tensor-geometry. In fact, hardly any formulæ appear at all.

The subject-matter originally constituted a set of University lectures intended not for the specialist, and it is perhaps a pity that the collection of a group of such lectures in this manner is not a more common event.

We can cordially recommend the book to any scientific library. It should be peculiarly adapted to stimulating the young student to pursue the subject in the more extended treatises.

*The Mechanical Properties of Fluids.* Blackie & Son. (Applied Physics Series.) 20s. net.

THIS is a joint work by nine authors, all of whom are experts in their respective subjects. It is, in some respects, a new departure which might well be followed in regard to other outstanding departments of Physics in which the literature at present is so deficient. It is perhaps difficult to secure the cooperation of a group of authors who are ploughing, in different directions, the broad acres of a subject closely related to some of the most fundamental things in direct technical practice. This volume at least is a brilliant success in this direction, and should prepare the way for others. It owes its inspiration to Admiral Sir George Goodwin, who is to be congratulated on the band of collaborators he has collected. It is intended primarily for engineers, but there are few mathematicians and physicists, however familiar with the current text-books on hydrodynamics, who could not learn much from its pages.

The account given of the most modern works which, as is well known, has tended so much to remove the reproach from ordinary theory of fluids that it has little relation to the behaviour of an actual fluid, is entirely up to date, and in fact written by the experts, such as Prof. Taylor, who are really responsible for the most significant advances.

The book is so arranged, and the amount of space devoted to each important aspect is so adjusted, that it can really serve as a text-book on hydrodynamics. Prof. Lamb's contribution especially bridges many gaps which would otherwise occur between the other articles.

The many subjects dealt with, apart from the general article of 45 pages on the mathematical theory of the motion of a perfect fluid, include such widely different things as viscosity and lubrication, the theory of gases, streamline flow and eddies, resistance of fluids to moving bodies, phenomena of fluid elasticity and the determination of stresses by the use of soap films, wind structure, and the practical applications of the properties of fluids involved in submarine signalling and the movement of projectiles.

The work is entirely to be recommended, and, it may well be hoped, is the forerunner of others of its class. It is an indispensable addition to any scientific library.

*Hydrodynamics.* By Prof. HORACE LAMB. (Fifth Edition.)  
Cambridge University Press. 45s. net.

THIS has for so long been the classical account of this subject that the appearance of a much enlarged fifth edition is no surprise. It would, indeed, be difficult at the present day to find a writer on any mathematical topic with the peculiar clearness and lucidity displayed in all the author's writings. A great amount of the work described was done, in the first place, by himself. Yet it is difficult for one not familiar with it to distinguish it in any way from that due to others, to which Prof. Lamb lends a lucidity and charm of expression only too frequently absent from the original accounts.

All serious students of the subject will already be sufficiently familiar with earlier editions. Work in a subject regarded, not many years ago, as 'dead,' has received the most extraordinary impetus in recent years, and it is now common to hear of 'real' hydrodynamics as against the classical theory,—a rebuke to the latter which is not often expressed with complete fairness. The reader of this edition will find both, and the manner in which the author has succeeded in incorporating the recent advances into what was already a very finished treatise, without producing, at any point, a sense of discontinuity in the mind of the reader, is a notable literary achievement.

The general form of the work is perhaps the final illustration of the excellence of the mathematical series of the Cambridge University Press. In a way difficult to define, and due at least in part to the author's judicious interpolations of prose and of formulæ, this volume is more pleasant to the eye than almost all the others in the series.

*X-Rays and Crystal Structure.* By Sir WILLIAM BRAGG and Prof. W. L. BRAGG. G. Bell and Sons. 21s. net. (New Edition, revised and enlarged.)

SUCH a work as this, needing a fourth edition so very soon after the third, and with the first only dating back nine years, clearly has a popularity and value which make a notice almost unnecessary. The alterations and additions which have been made alone call for detailed attention.

More exhaustive treatises have appeared recently, notably those of Dauvillier and Ewald, but the authors do not claim to be exhaustive. They, as authors of the first connected account of a new subject owing so much to their own work, are only seeking to preserve a connected account in such a manner that the influence of the most recent researches in a rapidly-developing subject shall be justly felt by the reader. It is very largely re-written and seems quite to supersede the older editions. Its scope is designed to be limited to the giving, to students of very diverse sciences, from mineralogy to physics, of a connected statement of the

present position of the subject and the methods by which it has been reached. The authors apologise for the somewhat fluid state of the terminology of the subject, which, whenever it seems fixed, is continually disturbed by a new piece of research,—and they instance Prof. Compton's work which no longer allows us to say that scattered radiation has the same wave-length as the original.

The work is full of excellent and really instructive diagrams, and its general aspect is very pleasing. We can only express the hope that further editions will be called for in the same limited periods.

*The Evolution of Mathematical Physics, being the Rouse Ball Lecture of 1924.* By HORACE LAMB, Sc.D., F.R.S., Fellow of Trinity College, Cambridge. (Cambridge, at the University Press.)

It is certainly a most fitting and happy choice which has made Professor Lamb the Rouse Ball Lecturer for 1924. After a long and strenuous teaching career which has revolutionized the teaching of Mathematical Physics and an equally strenuous life of Research which has marked out and illumined large territories in mathematical physics, Professor Lamb has returned to Cambridge, and any opportunity of hearing him is to be seized upon. In the course of this lecture, which we are very glad to have in print, a rapid survey is taken of the currents of mathematical physics, as developed by the great writers of the eighteenth and early nineteenth century. The starting point of mathematical physics is fixed by the publication of Poisson's first memoir on Sound in 1807—a year which is also memorable for the first instalment of Fourier's investigations on the Conduction of Heat, whose importance extends far beyond the special subject *a propos* of which the trigonometric series for ever to be associated with his name arose. The great flow of production from this time onwards is associated with a group of famous names: Oersted's discovery of the action of an electric current on a magnetic needle came in 1820; Ampère's work on the mechanical action between electric circuits followed soon after. The researches of Navier, Cauchy, and Poisson on Electricity were followed by Green's Essay on Electricity and Magnetism in 1828. Neumann, twenty years later, developed further the ideas of Ampère. Professor Lamb continues the thrilling story of nineteenth century mathematics and mathematicians, touching in turn on the work of Kirchhoff in Electric Induction, of Stokes in Diffraction, of Helmholtz in Vortex Motion, and on the remarkable work of Maxwell in many domains.

We can heartily recommend this lecture to the attention of mathematicians and physicists. It teaches the great lesson which was better known to the last generation than to the present generation, that "*l'étude approfondie de la nature est la source la plus féconde des découvertes mathématiques.*"

*A Comprehensive Treatise on Inorganic and Theoretical Chemistry.* By Dr. J. W. MELLOR. Vol. 5. (Longmans, Green & Co. 63s. net.)

THE fifth volume of this enormous undertaking is devoted to the elements Boron, Aluminium, Gallium, Indium, Thallium, Scandium, Cerium, and the rare earth metals to a smaller extent. To the treatment of the rare earths, a sequel is to follow.

The work proceeds on the same comprehensive lines as before. The only possible criticism is that it is by far too comprehensive—not in the sense of dealing with all known qualitative or quantitative phenomena relating to these elements, but in the sense that it includes too much literature. The feeling we had about earlier volumes is intensified by the study of this one,—that the discrimination between good and bad work among such a multitude of authors has not been carried out effectively. In fact, the author does not appear, in his plan, to include such an attempt. Consequently a student, turning to these pages for help in a given matter, may be overwhelmed by the wealth of references he will find, and the absence of any guidance to him as to which he should read and which he may ignore, at least in the first instance. The relative value of various views of any given topic might well be stated also in many instances.

But as a final work of reference, or as a dictionary of chemical literature and knowledge, the work is quite unrivalled. It has appeared very soon after the preceding volume, and it is perhaps hardly fair to expect an author, who has had the great courage required for an undertaking of this magnitude, and the untiring industry apparent in every page, to be able to go further on the lines we have mentioned.

There is at least no doubt that the presence of this series in a library will save it great expense, in the long run, on miscellaneous periodical literature, and will be of extreme value to readers.

*Alternating Current Rectification.* By L. B. W. JOLLEY. (Chapman and Hall. 25s. net.)

THIS is a very welcome book. The author is one of the research staff of the General Electric Company, with necessarily a large experience of actual rectifiers of many designs. In a very new subject such as this, with the enormous developments recently due to, for example, the introduction of the thermionic valve, it has been impossible for the new editions of ordinary works on electricity or even its technical engineering side to keep pace with progress.

This work completely fills the gap on the practical side as it now exists, though it would be difficult to say how rapidly the gap may continue to widen again. A very welcome feature is the use which the author has made of the patent literature, which, as a rule, requires a long time before it really influences text-books.

There is an abundance of useful diagrams of the apparatus described, and the work is pleasant to read, and very free from misprints. It will form a useful addition to the library of any electrical engineer, or certain types of specialist in electrical physics.

*Modern Astrophysics.* By Prof. H. DINGLE. (Collins, Sons & Co. Ltd. 30s. net.)

WE have long needed a comprehensive account of astrophysics, inclusive of all the newer views in a science which advances more rapidly today than almost all others, and has already ceased to be in any way a subsection of astronomy or of physics. An author of such a work has a great opportunity of giving a balanced survey of a subject in which, at every hand, it is possible to hold very different opinions and quote equally weighty experts on either hand.

We fear that the author has not seized this opportunity. The work is a mine of information which is only otherwise to be obtained by laborious search among scientific journals, and on this account alone it is of great value to a reader who wishes to learn the nature of the phenomena and some of the theories which have been proposed towards their elucidation. On the practical side, in fact, the work is not readily reproached. The account of the phenomena and of modes of investigation is excellent throughout, though written at times in a manner which vaguely suggests the theatre—the author is far too fond of filling the middles of his paragraphs with notes of interrogation.

In so far as he is clearly the type of worker who is not prepared to believe any thing which eyes have not seen in a laboratory, he is at least consistent, and a reviewer would not quarrel with his treatment. But this fact hardly justifies him in the implicit assumption that there is no phenomenon shown, for instance, by the spectra of celestial bodies, which cannot ultimately be reproduced in the limited space of a vacuum-tube. Nor is it appropriate to dismiss, as he does in several instances, investigations of a theoretical nature which are now, or have been, important, with the briefest of mention on the sole ground that the laboratory has given, as yet, no evidence for or against them. They should at least be effectively presented for the reader to have a chance to formulate his own view as to their merits.

The writer is clearly not a mathematician, but it is not investigations of this class alone to which we refer. He has, in fact, not given a really critical survey, but rather that of an advocate,—and not always a consistent one. But in spite of what must be regarded as defects, which may be remedied in future editions which are likely to be called for, we nevertheless would congratulate the author on a very difficult piece of compilation and on the production of what is, in effect, our first book dealing in a general way with the whole range of astrophysics. In the final chapter, on “astrophysics as it will be,” the author, as sometimes in earlier sections, is somewhat carried away by his own language, and ceases to be quite scientific.

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